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CONTAINING
THE PAPERS READ BEFORE THE SOCIETY,
AND
ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN OTHER JOURNALS.

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JOURNAL

OF

THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*Study of Hydrogen Dioxide and Certain Peroxides, including Experiments to determine the Heat of Formation of the Oxygen-molecule.*

By T. FAIRLEY, F.R.S.E.

I. PEROXIDE OF HYDROGEN AND METALS.

SINCE the discovery of hydrogen dioxide by Thénard in 1817,* its remarkable properties have excited much interest. That it should prove an energetic oxidising agent is what might be expected,† but there has been no inconsiderable difficulty felt in attempting to explain the numerous reactions in which it gives up half its oxygen in the free state, and in contact with other oxygen compounds even acts as a reducing agent. Thénard and Mitscherlich‡ considered that oxygen is given off in consequence of the development of heat,§ while Berzelius classed these phenomena with others, not explained by the electro-chemical theory, as examples of catalytic or contact action.|| He supposed that in all cases of catalysis the acting body did not itself undergo any change during the process. Liebig¶ modified the catalytic theory and compared the action of certain metals and oxides in

* *Ann. Chim. Phys.*, viii, xi; *Traité de Chimie*.

† *Gmelin's Chemistry*, Engl. Trans. II, 77; *Odling's Chemistry*, 123; *Watts's Dict.* III, 97.

‡ *Pogg. Ann.*, lv, 32.

§ I shall show that the converse is true.

|| *Berz. Jahresbericht*, xv, 287. The term "contact action" is due to Mitscherlich; *Pogg. Ann.*, xxxi, 281.

¶ *Ann. der. Chem.*, ii, 22; *Gmelin's Chem.*, Eng. Trans. I, p. 115.

causing the evolution of oxygen from hydrogen dioxide with that of pulverulent or angular bodies on liquids saturated with a gas. Dumas, Laurent, Graham, and many other chemists, have written on this subject, while the molecular theory,* as applied by Brodie, was shown to have a most important bearing on their explanation. The theory of atomic motion applied by Williamson† to the explanation of many cases of chemical action ought also to be here mentioned.

The reactions in which hydrogen peroxide or alkaline peroxides act as reducing agents, have been made the subject of elaborate investigations by Brodie,‡ and independently by Schönbein.§

Brodie considers that the molecule of oxygen set free in these reactions is formed by the union of two atoms in opposite polar states, the polarity being due to the previous combination of these atoms, and therefore not necessarily permanent, while Schönbein assumes the existence of permanently negative oxygen or ozone \bar{O} , and permanently positive oxygen or antiozone \bar{O}^+ . The true nature of ozone has however been demonstrated by the investigations of Andrews and Tait,|| Soret,¶ Brodie,** and others, while Meissner's†† results proving the existence of antiozone have been shown by v. Babo‡‡ to be doubtful, or at least requiring confirmation.

So far as I am aware, no one has attempted to improve on the theories of Berzelius and Liebig relating to the action of certain metals, charcoal and other substances in a finely divided state, in inducing by simple contact the decomposition of hydrogen dioxide, while the metals or other substances apparently suffer no change. I have therefore endeavoured to ascertain whether these reactions might not be examples of *recurrent chemical action*, of which the decomposition of alcohol into ether and water by means of sulphuric acid or other bodies (remaining unchanged at the end of the process), as explained by Williamson,§§ the formation of sulphuric acid from

* First applied in Chemistry by Avogadro, 1811; and Ampère, *Annales de Chimie*, 1814, viii, p. 434; *Tilloch's Phil. Mag.*, 1815, pp. 41, 109, 189.

† *Chem. Soc. Qu. J.*, vi, 110.

‡ *Phil. Trans.*, 1850, p. 759; 1862, p. 837; *Chem. Soc. J.*, xvi, 316; iv, 194; vii, 304.

§ *Annalen der Chemie*, cxvii, 38; cxxx, 95.

|| *Chem. Soc. Qu. J.*, ix, 168.

¶ *Ann. Ch. Pharm.*, cxvii, 38, and cxxx, 95; *Ann. Ch. Phys.* [4], vii, 113; *Jahresb.* 1865, p. 120; xiii, 257; 1867, p. 123.

** *Phil. Trans.*, 1872, p. 484.

†† *Jahresb.*, 1863, p. 126; *Chem. News*, x, pp. 2, 13, 49, 73, 97.

‡‡ v. Babo and Claus, *Ann. Ch. Pharm.*, cxl, 348; *Jahresb.*, 1866, p. 98.

§§ *Phil. Mag.* [3], xxvii, 350; *Chem. Soc. Qu. J.*, iv, 106.

sulphur dioxide, water and atmospheric oxygen by means of oxides of nitrogen, the manufacture of white lead by the old Dutch method, and the continuous oxidation of organic matter in contact with ferric oxide, &c., may be given as examples.

When hydrogen dioxide* even very dilute, is brought in contact

Action of
metals under
different
conditions.

* The hydrogen dioxide used in the following experiments was in some cases prepared by myself by Thénard's process, but as I found the dilute dioxide now manufactured for medicinal purposes to be tolerably pure, I preferred to save time by using the latter. Its strength varied from 2 to 5 per cent. of real dioxide. From the impurities present—free hydrochloric acid and barium chloride—I believe that it is generally prepared by Thénard's process.

The samples were carefully analysed in each case, and contained—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Water	96·57	95·47	94·013	94·49	96·17
(1.) Hydrogen dioxide	3·23	4·34	5·117	5·12	3·06
Hydrochloric acid	0·11	0·12	0·80	0·34	0·71
(2.) Solid residue consisting chiefly of barium chloride	} 0·09	0·07	0·07	0·05	0·06
	100·00	100·00	100·00	100·00	100·00
(1.) Equal to oxygen	1·52	2·12	2·408	2·41	2·24

	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Water	96·26	97·136	97·504	97·755	—
(1.) Hydrogen dioxide	3·23	2·757	2·39	2·21	5·95
Hydrochloric acid	0·22	0·070	0·08	0·018	—
(2.) Solid residue consisting chiefly of barium chloride	} 0·29	0·037	0·026	0·017	—
	100·00	100·00	100·00	100·00	—
(1.) Equal to oxygen	1·52	1·288	1·17	1·04	2·80

(2.) By means of argentic sulphate and barium hydrate solutions, these impurities are easily separated. In determining the oxygen in this and other peroxides described in this paper, I have found the titration in acid solutions with decinormal solution of pure potassium permanganate to be most accurate and convenient. The titration is accurate in clean glass or porcelain vessels, but not always in those of platinum. The permanganate should be added gradually, with constant stirring or shaking of the liquid. If the permanganate be run in very rapidly, an evanescent brown colour is sometimes observed where the liquids come in contact, and in these cases the results are under the truth. The acid used is preferably dilute sulphuric acid, of which an excess does no harm.

The titration in *alkaline* solutions by means of sodium arsenite gives results concordant among themselves, but always slightly below those obtained by permanganate in acid solutions. The indicator, iodide of starch, probably interferes.

with finely divided gold, silver, platinum, and other substances, there immediately commences a steady evolution of oxygen more or less rapid, according to the state of division of the metal, the degree of dilution of the liquid, the temperature, and according as the liquid is acid, neutral, or alkaline.

In acid solutions there is an exceedingly slow evolution of oxygen.

In neutral solutions the metals are often slightly discoloured,* and the evolution of oxygen is more apparent than with acid solutions.

In alkaline solutions the action is generally energetic, and the dioxide is rapidly decomposed, abundance of oxygen being given off. In alkaline solutions it is evident that, if the metals are at all oxidised during the decomposition of the dioxide, they cannot, in the majority of cases, pass into any more stable state of combination, but must remain as oxides until the latter are decomposed. It is otherwise, however, in acid solutions where the acid present can, by its action on the oxide, form with the metal a compound *more stable than the oxide* of the metal, for we have then little or no evolution of oxygen, and the metal quietly dissolves in the liquid.

New solvents
for gold,
silver, and
platinum.

Thus, finely divided silver placed in a 10 per cent. solution of sulphuric acid to which a 2 per cent. solution of hydrogen dioxide has been added, gradually and quietly dissolves, forming a solution of argentic sulphate. If the liquid be moderately heated, or if a stronger acid be used, the metal dissolves much more rapidly. The results are similar with other dilute acids, such as *dilute* acetic, formic, oxalic, nitric, &c.

A mixture of a 5 per cent. solution of hydrogen dioxide and a 10 per cent. solution of sodium hyposulphite also readily dissolves silver, especially if in a finely divided state, and similarly, if a solution of potassium cyanide be used in place of the hyposulphite. In each case a sensible development of heat is observed, and the alkaline reaction of the reagents remains unchanged during the process.

In every instance where an acid or other substance is present capable of forming with silver a compound *more stable than argentic oxide*,† and not decomposed in aqueous solution, the metal quietly dissolves, the proportion of hydrogen dioxide diminishes, and little or no evolution of oxygen takes place.

I may point out, as somewhat interesting, the dissolution of silver

* Weltzien, *Ann. Ch. Pharm.*, cxlii, 105; cxxxviii, 129. *Jahresb.*, 1866, 107; *Ch. News*, xiii, 159; xiv, i, 15, 39, 50. *Suppl. Watts's Dict.*, 1872, 719.

† Since this paper was read, I have ascertained that with finely divided silver even this limitation may be removed. On adding hydrogen dioxide to a 10 per cent. solution of sodium hydrate containing the silver in suspension, oxygen is rapidly evolved and the metallic residue contains a large proportion of oxide of silver.

in very dilute formic acid. This solution, generally regarded as very unstable, I have kept for months without apparent change, and at the end of the time it still contained free hydrogen dioxide and formic acid.

The number of salts of gold and platinum which are more stable than the oxides is very limited. I have, however, dissolved these metals in a mixture of hydrochloric acid and hydrogen dioxide. The acid should be in large excess, as I have also observed the precipitation of metallic gold from a solution of crystallised auric chloride and hydrogen dioxide, after standing for some time.* An auric peroxide which I have hitherto failed to isolate is probably first formed, but in three experiments the precipitate obtained by addition of hydrogen dioxide to solution of pure crystallised auric chloride, after drying at ordinary temperatures, consisted simply of metallic gold.

This metal also dissolves readily in a mixed solution of potassium cyanide and the dioxide. The same solution of the cyanide had no effect on gold by itself, except at the surface of the liquid.

A solution of ferric chloride† also dissolves gold in the state of gold leaf after addition of hydrogen dioxide. If a slight heat be employed, the action appears to be at first facilitated, and is sometimes followed by a reprecipitation of the gold.

The presence of hydrogen dioxide interferes with the precipitation of gold from its solutions by means of ferrous sulphate or oxalic acid. The dioxide must first be decomposed before these reagents can be used to precipitate the gold.

As might be expected, mercury, copper, and other metals dissolve with increased facility in acids containing hydrogen dioxide. No gaseous products of deoxidation, &c., are evolved in those cases where they would otherwise be obtained, and the metals dissolve quietly without losing their metallic brilliancy. These facts are well shown in the case of metallic copper and nitric acid.

Where acids are employed which form insoluble salts with the metals, these salts are formed: thus silver and mercury with hydrochloric acid and hydrogen dioxide form argentic and mercurous chlorides. The latter is only very slowly changed to mercuric chloride, even if heat be employed.‡

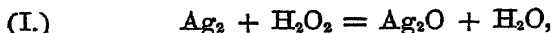
These observations may help us to explain the so-called catalytic

* There is probably a *dissociation* of the gold salt in the dilute solution, a portion of auric oxide being formed.

† The ferric chloride used in these experiments contained an *excess* of base, viz., in 100 parts of dry substance, FeCl_3 91.88, and Fe_2O_3 8.12, giving the ratio 88.28 Fe : 61.72 Cl. The formula FeCl_3 requires 34.46 Fe : 65.53 Cl. It contained no *ferrous* salt and no other acid.

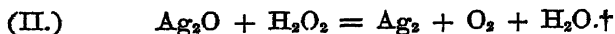
‡ This fact is in striking contrast to the effect of hypochlorous acid and hypochlorites on mercurous chloride, which is the basis of a method proposed by me for separating mercurous salts from those of lead and silver.

action of certain metals on the dioxides of hydrogen and the alkali-metals. There is first an oxidation of the metal: thus with silver, argentic oxide is formed,*



and then the oxide enters into reaction with the acid or other substance present.

In neutral or alkaline liquids where oxygen is more abundantly given off, there is a decomposition of the metallic oxide with formation of metal, ordinary oxygen, &c. Thus—

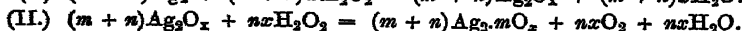
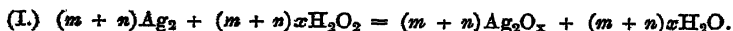


That, even in presence of excess of alkali, platinic oxide may be formed is well shown by heating sodium peroxide on platinum, when the dark stain and the precipitation of platinum on addition of water to the mass, prove that corrosion has taken place. Wherever corrosion of platinum or silver takes place by heating in contact with alkaline hydrates, it is probably due to this cause. By heating on platinum, an intimate mixture of potassium chlorate and sodium hydrate, corrosion of the metal is also observed.

II. HYDROGEN DIOXIDE AND METALLIC OXIDES.

The facts of preliminary oxidation shown to occur both in acid and in alkaline solutions when certain metals are treated with hydrogen dioxide, or alkaline peroxides, bring the phenomena of the contact action of these metals within the same class as the reducing action of the dioxide on the metallic oxides. The theory of Brodie (*Phil. Trans.*, 1850, p. 759; 1862, p. 837), based on the polarity of the atoms at the moment of chemical change, and Williamson's theory of atomic motion (*Chem. Soc. Qu. J.*, vi, 110), seem to me more per-

* The exact degree of oxidation is immaterial to the argument. For writing equations (I) and (II) in a general form, let m , n , and x be any positive integers. then—



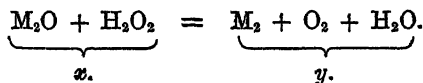
Weltzien describes the formation of argentous oxide Ag_2O by the action of H_2O_2 on a silver plate in perfectly neutral solutions (*Ann. Ch. Pharm.*, cxlii, 105), and he further states that the silver residue, from the action of H_2O_2 and Ag_2O , consists of this suboxide. My analyses of this residue in a great number of experiments show that its composition is exceedingly variable. A few of these analyses are quoted in the calorimetric experiments, p. 20.

† Argentic peroxide may also be formed though transient. I have obtained a crystalline double peroxide of silver and ammonium.

fect explanations of this kind of reaction than any others of which I have been able to find an account.

The following attempt to consider these phenomena in relation to the transmutations of energy involved in the reactions does not involve anything inconsistent with either of these theories:—

Let M be a metal or element whose oxide is reduced under given circumstances in contact with hydrogen dioxide; then in the equation—

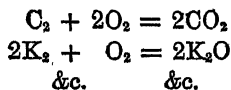


Let x = the total energy due to the formation *from the atoms* of the compounds M_2O and H_2O_2 measured approximately by its equivalent in heat-units; Energy due to reactions.

and let y = the total energy due to the formation *from the atoms* of the bodies M_2 , O_2 , and H_2O , also measured in heat-units;

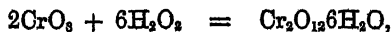
then, if y be greater than x , the change indicated by the equation will occur and give rise to heat equal to the equivalent of $y - x$ in heat-units.

The measurement of the quantity of heat produced in reactions involving the formation of oxygen-molecules must, as in all other cases, be a measure of the excess of work spent after the change over that spent before it. If, therefore, heat is produced by these reactions, there is the same reason why they should occur as the well-known reactions—



In each of these the heat observed is the measure of the excess of the energy due to the formation of the new compounds over that due to those previously existing.*

Another mode in which we may profitably study these reactions, and which is not inconsistent with the previous views, is to suppose that the selective character of hydrogen dioxide in acting more readily on some oxides than on others, may be due to the formation of very unstable highly oxidised compounds by the union of the dioxide with the oxide used. Brodie's experimental results led him to state this view as probable in the reactions of chromic and permanganic acids with the dioxide. He suggested that



* In other words the peroxide reactions resemble these others in their analogy to a falling weight, a bow unbending, &c.

chromic acid and hydrogen chloride might form a new oxide, and that



permanganic acid and hydrogen dioxide might also form a new oxide.

The gradual nature of the decomposition of hydrogen dioxide with chromic and permanganic acids, especially at low temperatures, is suggestive of the existence of these higher oxides, while the new uranium compounds described by me in this paper possess strictly analogous formulæ.

Now if we assume that in those cases where hydrogen dioxide readily acts on oxides, causing reduction, there are first formed unstable compounds which rapidly decompose at ordinary temperatures in aqueous solutions, we can understand that such oxides as have little tendency to unite with hydrogen dioxide *should not be reduced by it*. This view is supported by the formulæ of the new uranium compounds, which are less unstable than others on account of the high *atomic weight of uranium*, and by the discovery of new crystalline compounds of molybdenum, tungsten, silver, gold, and other metals, which are now being investigated.

III. THERMO-CHEMISTRY OF THE OXYGEN-MOLECULE.

The truth of the theory of molecules as distinct from atoms is now, from the results of numerous researches, chemical and physical, fully established, and plays an important part in modern scientific theory. I do not know that it has yet been *practically* applied in thermo-chemical researches.

Thus, in the equation representing the union of molecules of hydrogen and chlorine to form molecules of hydrochloric acid.



Energy due
to formation
of hydro-
chloric acid.

Let x = the molecular energy due to the union of one gram of hydrogen atoms with another gram of the same atoms; to form 2 grams of hydrogen-molecules, this energy being supposed to be transmuted into heat and measured in heat-units;

let y = the energy due to the union of 71 grams of chlorine atoms in pairs to form molecules, measured by its equivalent in heat-units;

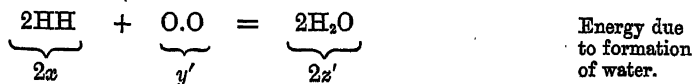
and z = the energy from the union of one gram of hydrogen atoms with 35.5 grams of chlorine atoms to form 36.5 grams of hydrochloric acid—assuming this energy to be transmuted into its equivalent in heat-units.

Then, according to the results of Andrews, Favre and Silberman, and Thomsen, &c. (*Miller's Chemical Physics; Watts's Dictionary of Chemistry*, iii, 117; 2 Suppl. 1875, p. 608).

$$z - \frac{x + y}{2} = 22,000 \text{ gram degrees.}$$

If x and y be considerable as compared with z , this equation cannot afford any approximation to the real value of the latter.

Similarly in the formation of water:—



Let x , y' , z' represent the respective energies measured as before, then $z' - x - \frac{y'}{2} = 68,360$ gram degrees. Unless we assume x and y' to be very small compared with z' , the equation cannot give any approximation to the value of z' .

I have sought to obtain approximations of the value of y' (i.e., the Method of energy due to the union of the atoms of oxygen to form the molecules approximating to the energy of the reactions of unstable oxygen compounds studied in this paper, and I hope to apply the same method to the elements hydrogen and chlorine, molecule, &c. to obtain an approximate solution of the above equations.

I make the following general observations, founded on the strict analogy of the energy due to chemical attraction with all the other known forms of energy.

1. The energy due to the union or falling together of atoms must, under any circumstances, where such union can take place, be a *positive quantity* (just as the energy due to falling of masses to the earth is a positive quantity), which can be measured approximately by its equivalent in heat-units.

2. That the union or falling together of atoms cannot give rise to an absorption of heat any more than the falling together of masses, such as bodies to the earth can give rise to an absorption of heat.

3. That there can be no work done by chemical separation or decomposition any more than work can be done by a body rising from the earth while it is rising, but that in either case work is spent on the atoms separated or the body raised. If any given quantity of a chemical compound in decomposing causes the production of so many heat-units, these must be due *not to the separation*, but to the *union* of the atoms in new combinations, the heats of formation of which prevail over those absorbed by the decomposition of the original compound.

4. That from the above, the energy due to the union of atoms must

be greater, *ceteris paribus*, the greater the number of atoms uniting. If m number of A atoms unite with n number of B atoms to form the compound $A_m B_n$, their union must develop more heat than the union of any smaller number such as $A_m B_{n-1}$. Thus the heat of formation of hydrogen dioxide *must be greater* than the heat of formation of water; or where the atoms are of one kind, the heat of formation of ozone O_3 must be *greater* than the heat of formation of ordinary oxygen O_2 , &c.

Energy due
to the forma-
tion of H_2O_2
and of O_3 .

The bodies H_2O_2 and O_3 are observed to be formed (a) in certain processes of slow oxidation; (b) by the action of the electric discharge on oxygen*; (c) by the electrolysis of water. The atoms of oxygen are separated either from the molecules of ordinary oxygen or from those of water, and immediately unite with the atoms or molecules in their neighbourhood. In cases of rapid combustion they are entirely taken up by the burning body†, while in cases of slow oxidation they only partly unite with it. In this latter case part of the atoms separated no doubt reunite, giving out the energy as heat which was absorbed in their separation; while another part unite with molecules of oxygen O_2 , and water H_2O to form ozone O_3 and hydrogen dioxide H_2O_2 , and give out a *much less amount* of heat (but still a *positive amount*, however small it may be); while the remaining portion of the heat absorbed in the separation of the atoms is set free when these bodies are decomposed into ordinary oxygen or oxygen and water. A similar explanation applies to the formation of oxides of nitrogen and the heat observed in their decomposition.‡

It is obvious that the more unstable the oxygen compounds the nearer will the heat observed during their decomposition approximate

* It has been shown that in preparing ozone by the electric discharge, the oxygen or air should be dry in order to gain the maximum effect, which may be explained by the action of H_2O_2 and O_3 on each other. $H_2O_2 + O_3 = 2O_2 + H_2O$.

† It is, however, possible to obtain ozone from an ordinary Bunsen rose burner. This fact I observed in 1870. The fact has also been recorded by Loew, *Zeitsch. f. Chem.* [2], vi, 65, 269.

‡ Since this paper was read I have found that M. P. A. Favre, opposing Berthelot's idea of "corps explosifs," explains the heat observed in the decomposition of nitrous oxide as follows:—"Le protoxyde d'azote $AzO\frac{1}{2}$ = 2 vol. se décompose, d'abord en $Az = 2$ vol. et en $O = 2$ vol., comme dans le composé dont O se sépare, ce qui constitue un premier phénomène qui est *thermonégatif*. A ce phénomène de ségrégation succéderait un phénomène d'agrégation, les 2 volumes d'oxygène se condensant en 1 volume; de là, un second phénomène qui est *thermopositif*, et qui l'emporte sur le premier." (*Annales de Chimie*, 1873, xxix, p. 90). This explanation, though greatly in advance of the ideas of Berthelot, involves assumptions of volume-changes, for which no proof is given, to prove what can be proved equally well without them.

Ener-
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to the real quantity of heat due to the union of the atoms to form molecules. It is also evident that, if this heat be comparatively large, the atoms must be far more active than the ordinary molecular form of the elements, and this explains and agrees with the peculiar power shown by elements in the nascent state.

Referring to the reactions of oxygen compounds which are here studied, the following hypothesis may be stated in accordance with the preceding observations :—

In each case where oxygen is evolved, heat is produced, and this heat is *a part* of that due to the union of the atoms of oxygen to form the molecule O_2 . The observed heat is probably in all instances less than the real value.

For the special objects of this enquiry I wished to avoid contact of metals with the liquids used, and therefore calorimeters of glass were employed. The tall beakers having a height equal to thrice their diameter, are suitable and convenient. In a nest of three of such beakers, the two smaller A and B, Fig. 1, having capacities of 200 c.c. and 400 c.c. were used as calorimeters. The smaller (A) when it was used was supported inside the larger (B) by a collar of cotton wool.* The third and largest of the three beakers (C) was coated with tinfoil on its *inner* surface (cemented thereto by means of paraffin wax) up to 2 c.m. from the lip, where a collar of cotton wool was placed between the second and third beakers. The tinned beaker (C) was placed in a large beaker (D) of the ordinary shape by means of abundant wrappings of fine cotton wool, and the latter again placed in a still larger beaker (E) covered with tinfoil on its *outer* surface, the space between the two outer beakers being filled with water. The calorimeter was covered by lids of tinned card-board, into which the thermometer and pipettes were fitted by corks (Fig. 2). The thermometer employed had a fine graduation from 0° to 30° C.; so that $\cdot 01$ of a degree could be read by means of a telescope. (Fig. 3.)

In each experiment one of the two liquids used was weighed out in the calorimeter; while the other was contained in a pipette so arranged that the liquid could be measured and weighed in the pipette, which could then be placed in the other liquid in the calorimeter without mixing. The pipettes used were of two forms (G and F, Fig. 2), the first having its lower extremity drawn out into a long, stout capillary S-tube, with the upper bend above the bulb of the pipette, and the second having the bent tube internal as shown in the figure (F). These pipettes could be filled and weighed without using a compression tap to close their upper extremity. The liquids having been weighed and the cover with the thermometer and pipettes placed in position in the calorimeter, the latter with its casings is placed in the centre of a

* The variety sold under the name of "jeweller's wool."

Apparatus
and method
used.

table, having clamped to it at one end a stout pillar bearing the telescope (H, Fig. 3). After allowing sufficient time for all parts of the

FIG. 1.

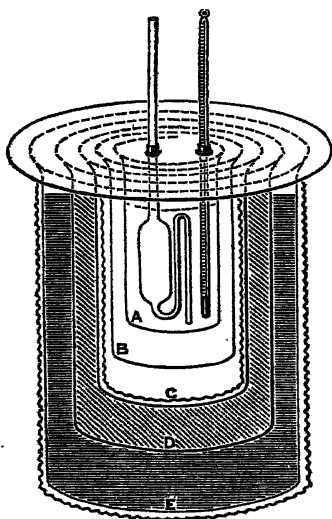
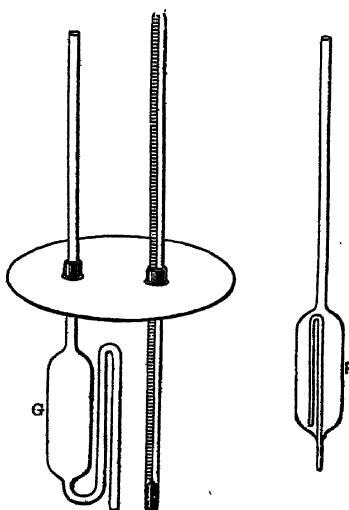


FIG. 2.

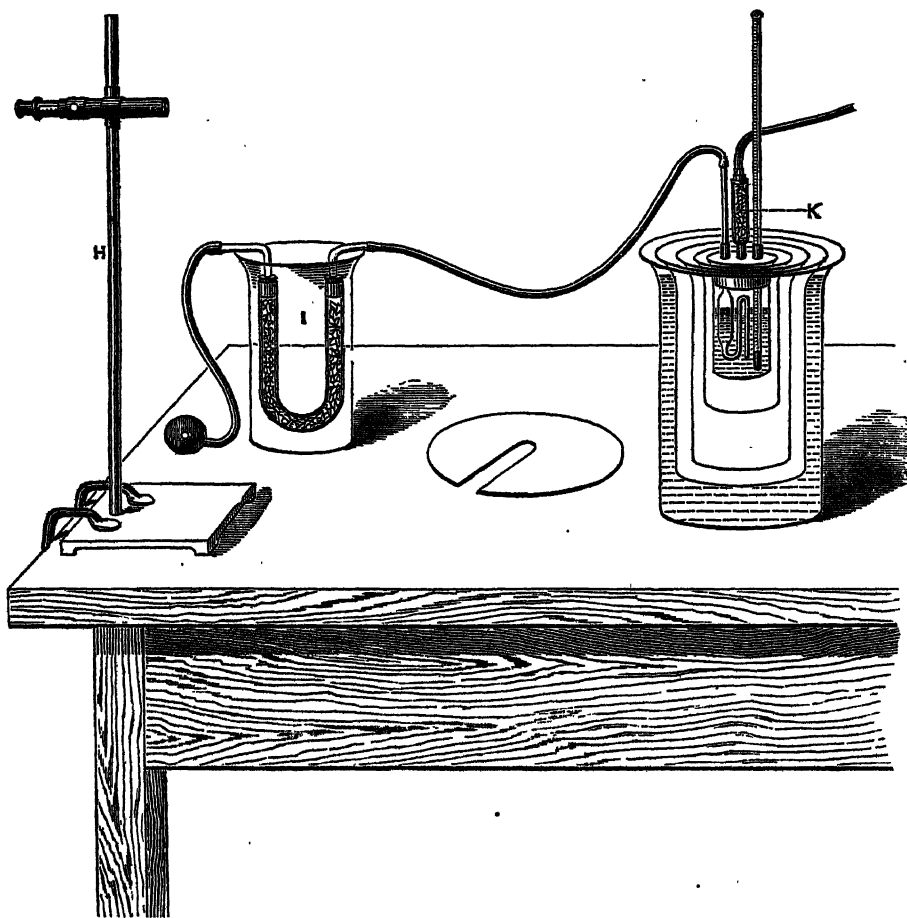


calorimeter to attain a constant uniform temperature, the thermometer is read off. The pipette is now emptied by compression of an india-rubber ball previously attached to it, or by means of aspirating bottles connected so as to blow into it. The capacity of the pipette being known, one can blow in just sufficient air first to empty it, and then to thoroughly mix the liquids. While using the india-rubber ball, the observer looking through the telescope notes the thermometer. By adjusting the position of the latter so that the column of mercury can be seen as a dark line not upon the graduation, but close beside it, the readings can be made much more exact.

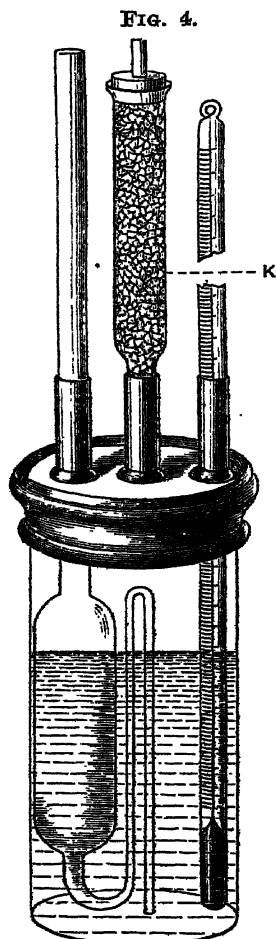
The above method gives fairly accurate results with the means at my disposal, and is applicable in all cases where the oxygen given off can be accurately calculated from the composition of the materials used. In the case of certain metallic oxides, such as oxide of silver in suspension in a neutral or preferably an alkaline liquid, it is not possible beforehand to calculate accurately the amount of oxygen evolved from the oxide, and either the loss of weight of the calorimeter with its fittings, must be observed so as to ascertain the weight of oxygen evolved, or this weight may be calculated from the analysis of the metallic residue remaining in the calorimeter. In the case of argentic oxide I have tried both methods many times. They seldom

agree, and of the two I consider that the latter method gives the more accurate results. The determination of the oxygen by the direct loss of weight of the calorimeter is affected by the fact that

FIG. 3.



the liquid remaining in the calorimeter is often really a supersaturated solution of oxygen, which only very slowly gives off its excess of dissolved gas. When this method was adopted, the air blown into the pipette was carefully dried by passing through the chloride of calcium tube (I, Fig. 3), and the escaping gas was also dried by passing through another chloride of calcium tube (K, Figs. 3 and 4). The thermometer, pipette, and exit-chloride of calcium tube



were in these experiments fitted into three tubulures of a stout india-rubber cap, stretched over the mouth of the beaker (Fig. 4). A thin cork placed within the cap, and with holes corresponding to the tubulures, secured the thermometer and pipette in position.

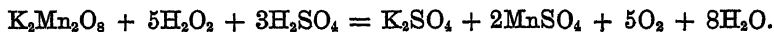
In order to check the results obtained by the use of these small beakers as calorimeters, I made special experiments, using the two outer large beakers (D and E, Fig. 1) as a calorimeter, the space between them being packed with cotton-wool. The beaker (D) was of about 2,500 c.c. capacity, and could therefore be worked conveniently with 2,000 c.c. of liquid. Any loss of temperature due to heat carried off by the escaping gas would in this apparatus be reduced to a minimum, and the total rise of temperature being often only a fraction of a degree, the loss by radiation, &c., during an experiment would be inappreciable. With this large calorimeter it was necessary, before finally reading off the temperature, to mix the liquids thoroughly by stirring with the pipette.

In calculating the results, the data required in order to ascertain the heat due to the evolution of 32 grams of oxygen are:—

Weight of water or liquid in calorimeter ..	= W
Specific heat of liquid in calorimeter	= S
Water value of calorimeter and fittings	= V
Initial temperature (centigrade)	= T°
Final temperature	= t°
Weight of oxygen evolved determined by analysis and calculation	= M
Weight of oxygen evolved determined by loss of weight of calorimeter	= m
Heat-units (gram-degrees) due to the forma- tion of one molecule of oxygen in grams (i.e., 32 grams)	= H

$$\text{then } (W \times S + V)(T^\circ - t^\circ) \frac{32}{M \text{ (or } m)} \dots = H.$$

In many cases other reactions take place simultaneously, but it is, I think, very probable that the heat due to these is generally less than that absorbed by the decomposition of the original compounds. Thus in the reaction—

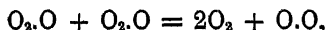


The heat due to the change of potassium permanganate into potassium sulphate is eliminated by mixing the acid and permanganate first, and before the initial temperature is read, while the heats of formation of the manganese sulphate and other secondary reactions are probably less than that absorbed in the decomposition of permanganic acid, hydrogen dioxide, &c., so that the observed heat is less than the real heat due to the formation of the oxygen.

Thomsen, in his extensive thermo-chemical investigations, has determined the heat due to the decomposition of hydrogen dioxide in contact with platinum-black as 46,140 heat-units for each 32 grams of oxygen evolved, while Favre and Silbermann, whose experiments were necessarily less accurate, found 43,616 heat-units. Results obtained by others.

Thomsen has also determined the heat due to the reaction of permanganic acid and hydrogen dioxide, and his results and mine agree as closely as might be expected (*Deut. Chem. Ges. Ber.*, vi, 239; *Watts's Dict.*, 2 Suppl., p. 615).

Hollmann* has determined the heat due to the decomposition of ozone into ordinary oxygen. He found that 1 gram of ozone in passing into ordinary oxygen gives out 355.5 units of heat. Calculating this according to the equation for 96 grams of ozone—



we obtain the value 34,128 heat-units. Either the heat absorbed in the decomposition of ozone is considerable, or Hollmann's result is much below the truth.

Schönbein showed that hydrogen dioxide and arterial blood decompose each other, and Dewar and McKendrick proved that ozone and arterial blood also decompose each other: oxygen is evolved in both cases, but the thermal changes have not been observed.

Calorimetric Experiments with H₂O₂ and other Substances.

Up to the present time I have studied the reactions of hydrogen

* I have not been able to consult Hollmann's original paper (*Arch. Néerland.*, iii, 260); only very brief notices are given in *Jahresb.*, 1868, p. 99, and *Watts's Dict. Suppl.*, p. 894.

dioxide with permanganic and chromic acids, with argentic oxide, and with sodium hypochlorite.

The following experiments with permanganic acid may be quoted:—

(I.) Taken in beaker:—

Water	50.04 grams.
H ₂ SO ₄ dilute 12.16, containing real H ₂ SO ₄	8.41 „
K ₂ MnSO ₄ solution 10.5235, containing KMnO ₄	0.8035 gram.

Taken in pipette:—

H₂O₂ dilute 4.0832, containing H₂O₂, 0.1632 gram.
 Initial constant temperature, 20° C.; final, 22.2° C.
 Oxygen contained in permanganate, 0.0768 gram; in the dioxide,
 0.03 gram.
 Specific heat of the liquid, 0.956; water value of calorimeter,
 8.98 grams.

$$H = (76.807 \times .956 + 8.98)(2.2) \frac{32}{1536} = 37,769 \text{ gram-degrees.}$$

(II.) Taken in beaker:—

Water	298.34 grams.
H ₂ SO ₄	3.71 „
KMnO ₄ solution, 10.5497 grams, containing	
KMnO ₄ , 0.3322 gram. oxygen, equal to..	0.0841 gram.

Taken in pipette:—

Dilute H₂O₂, 4.9 grams, containing oxygen.. 0.0892 gram.
 Initial constant temperature, 23.34° C.; final, 23.95° C.
 Specific heat of the liquid, 0.99; water-value of calorimeter,
 15.22 grams.

$$H = (312.5 \times .99 + 15.22)(.61) \frac{32}{1632} = 37,670 \text{ gram-degrees.}$$

(III.) Taken in beaker:—

Water	99.93 grams.
H ₂ SO ₄ dilute, 12.059 grams, containing	
H ₂ SO ₄	3.72 „
KMnO ₄ solution, 10.56 grams, containing	
oxygen.....	0.0841 gram.

Taken in pipette:—

H₂O₂, 5.01 gram, containing oxygen 0.100 gram.
 Initial temperature, 19.4° C.; final, 20.9° C.
 Specific heat of the liquid, 0.97; water-value of calorimeter,
 8.98 grams.

$$H = (127.559 \times .97 + 8.98)(1.5) \frac{32}{1682} = 37,872 \text{ gram-degrees.}$$

These and the following experiments with permanganate may be tabulated:—

Permanganate Experiments.

		W.	S.	V.	T° C.	t° C.	M. grams.	m. grams.	H. gram degrees.
KMnO ₄	(1)	76·807	·956	8·98	22·2	20	·1536	—	37769
"	(2)	812·5	·99	15·22	23·95	23·34	·1682	—	37670
"	(3)	127·559	·97	8·98	20·9	19·4	·1682	—	37872
"	(4)	68·88	·98	8·98	27·4	24·96	·16	—	37327
"	(5)						—	·155	39815
"	(6)	90·97	·995	15·22	24·92	20·49	·4	—	37472
"	(7)						—	·38	39182
"	(8)	71·02	·98	15·22	26·2	20·5	·41	—	37736
"	(9)	71·44	·98	15·22	27·5	21·83	·408	—	37902
"	(10)						—	·39	39652
"	(11)	71·32	·98	15·22	27·51	21·69	·42	—	37741
"	(12)						—	·393	40834
"	(13)	2070	·9994	57·38	17·29	17·05	·4205	—	38831
K ₂ Cr ₂ O ₇	(14)	2045	·9994	57·38	18·35	18·19	·305	—	35236

Experiments Nos. 5, 7, 10, 12 were performed by calculating the oxygen evolved from the loss of weight of the calorimeter. A certain amount of oxygen, more or less, remains dissolved in the liquid, as already explained, and hence these results are higher than the others. Experiment No. 13 was performed in the large beaker, as the non-conducting envelope was necessarily less perfect, and as the temperature of the air was about 17·5° C., while the mixing process occupied about one minute, it is probable that the number calculated from it is in excess.

Bichromate Experiment, No. 14.

This was performed in the large calorimeter; the result is simply given as approximate. The oxygen evolved from the bichromate with excess of H₂O₂ was calculated according to the ratio, 1 from bichromate to 2 from dioxide.

Argentic Oxide Experiments.

These were found to be more difficult than any of the others. Under no circumstances hitherto tried has it been found possible to reduce the whole of the argentic oxide present, even when a large excess of hydrogen dioxide was used. The recurrent action of the silver is so rapid and immediate, that even where attention was specially given to uniform mixing of the liquids at the expense of accurate observation of the change of temperature, a large proportion of unchanged argentic oxide was found in the residue. The highest ratio of reduced silver ever

observed was where 1.16 gram of silver in the form of argentic oxide (viz., 1.24 gram Ag_2O) gave 0.47 gram of reduced silver.

The argentic oxide used in each experiment was freshly precipitated as shortly as possible before it was made. The most convenient method was found to consist in the addition of the proper quantity of pure sodium hydrate solution to a decinormal solution of pure nitrate of silver. This precipitation was performed in the calorimeter, and allowance made for the nitrate of sodium present in calculating the specific heat of the liquid.

One experiment may be quoted in detail in which an attempt was made to secure more perfect reduction of the argentic oxide by mixing solution of argentic nitrate and hydrogen dioxide in the beaker, while sodium hydrate solution was placed in the pipette, so that the argentic oxide might react with the dioxide at the moment of its precipitation. The heat observed would be increased by that due to the precipitation of argentic nitrate by sodium hydrate, and it was therefore necessary to ascertain the correct value of the latter.

Thomsen gives, for the neutralisation of 2HNO_3 by 2NaHO , 27,360 heat-units, and for the neutralisation by Ag_2O , 10,880, giving a difference of 16,480 for the equation $2\text{AgNO}_3 + 2\text{NaHO} = 2\text{NaNO}_3 + \text{Ag}_2\text{O} + \text{H}_2\text{O}$. Andrews' experiments give for this equation 14,200, and those of Favre and Silbermann 18,308. As these values differ considerably, I have determined it myself directly.

Taken in the beaker, 101.099 grams AgNO_3 solution, containing 1.7 gram AgNO_3 .

Taken in the pipette, 10.03 grams NaHO solution, containing 0.4 gram NaHO .

Initial constant temperature before mixing, 20.3°C .; after mixing, 21°C .

Specific heat of the liquid, .994; water value of the calorimeter, 8.98.

Water value of the Ag_2O precipitated = $1.16 \times 0.047 = .0545$ gram. Therefore, heat due to the above equation:—

$$h = 110.239 \times .994 + 1.16 \times .047 + 8.98 \times .7 \times \frac{232}{1.16} = 16,605.$$

Two other experiments gave 16,479 and 16,368. The mean of these three numbers is 16,484, practically the same as that given by Thomsen, and this number was taken as correct, and employed in the following experiment:—

Taken in beaker:—

AgNO_3 solution, 50.52 gram, containing AgNO_3 .. 0.85 gram
equal to .58 gram Ag_2O .

H_2O_2 solution, 15.06 gram, containing H_2O_2 0.36 gram

Taken in pipette :—

NaHO solution, 5.593 gram, containing NaHO .. 0.24 gram

(On placing the pipette F, Fig. 2, with its contents, in the silver solution, both liquids remained clear; only a minute trace of argentic oxide could be observed in the capillary tube of the pipette, proving the perfect working of the instrument in these experiments.)

Initial constant temperature 21.4° C.; final, 24.7° C.

Loss of weight of the calorimeter = m = 0.176 gram.

Metallic silver reduced = .194 gram silver, equivalent to 0.014 gram oxygen.

Water value of calorimeter = 10.96; specific heat of the liquid, 0.997.

Water value of silver ($= .194 \times .057$), and of the silver oxide ($= .372 \times .047$), equal together 0.28 gram.

$$H = [(70.597 \times .997 + .028 + 10.96)(24.7 - 21.4) - \frac{16480}{400}] \cdot \frac{32}{176},$$

$$= 39,970 \text{ gram-degrees.}$$

or, calculating the oxygen evolved from that contained in the H_2O_2 and Ag_2O reduced = .182 gram.

$$H = [(70.597 \times .997 + .028 + 10.96) \times 3.3 - 41.2] \cdot \frac{32}{182},$$

$$= 41,333 \text{ gram-degrees.}$$

Argentic Oxide Experiments.

	W.	S.	V.	T°.	F°.	' (T-f)°.	M. grm.	m.	H.	Ag ₂ O taken.	Ag found.	Oxygen from Ag ₂ O H ₂ O ₂ .
(1)	70.625	.997	10.96	24.7	21.4	8.8	.182	—	39970	.58	0.19	.014 .168
(2)	"	"	"	"	"	"	—	.176	41333	"	"	" "
(3)	71.22	.992	8.98	26.05	24.5	1.55	.096	—	41132	.58	0.0594	.0045 .0915
(4)	71.89	.992	8.98	26.13	24.6	1.53	.0955	—	41162	.58	0.0548	.0041 .0914
(5)	"	"	"	"	"	"	—	.094	41819	"	"	" "
(6)	71.37	.992	8.98	24	22.42	1.58	0.974	—	41048	.58	0.0792	.0059 .0915
(7)	"	"	"	"	"	"	—	.095	42191	"	"	" "
(8)	91.12	.997	10.96	29.25	24.09	5.16	0.4	—	42027	.58	0.194	.0144 .3856
(9)	"	"	"	"	"	"	—	0.3975	42291	"	"	" "

As with the permanganate experiments, where the oxygen was determined by the loss of weight, higher values are obtained, and probably from the same reason. Lower values were obtained in the less accurate experiments not reported, where the proportion of argentic oxide reduced was greater.

Hypochlorite Experiments.



These were performed in the same manner as the permanganate experiments. Attempts made to eliminate the heat, probably due to the more complete neutralization of the sodium hydrate by the conversion of sodium hypochlorite into sodium chloride by previous neutralization of the base present, were, after several apparently successful experiments, found to be vitiated, as chlorine was evolved along with the oxygen, and I have therefore not reported these experiments.

The following may be quoted:—

(I.) Taken in beaker:—

NaClO solution 11·0462 containing	NaClO.....	0·447 gram
	NaCl	0·351 „
	NaHO.....	0·515 „
	water	9·7332 grams
Water		49·8494 „

Taken in pipette:—

H_2O_2 solution 8·9449, containing H_2O_2 0·1551 gram

Therefore oxygen contained in NaClO = 0·073 gram and in H_2O_2 = 0·0832 gram.

Initial temperature 21·85° C., final 24·2° C.

Oxygen determined by loss of weight = 0·14 gram.

Specific heat of the liquid, 0·98; water-value of the calorimeter, 8·98 grams.

$$H = (69·84 \times \cdot 98 + 8·98)(24·2 - 21·85) \cdot \frac{32}{146} = 39,878; \text{ or if we take the loss of weight,}$$

$$H = (69·84 \times \cdot 98 + 8·98)(2·35) \cdot \frac{32}{14} = 41,587 \text{ gram-degrees.}$$

(II.) Taken in beaker:—

NaClO, solution 11·05, containing NaClO	0·3609 gram
Water	93·05 grams

Taken in pipette:—

H_2O_2 , solution 5·5953, containing H_2O_2 0·1853 „

Therefore oxygen in NaClO = 0·0775 gram

in H_2O_2 = 0·0873 gram

Initial temperature = 21·55° C., final 23·12° C.

Specific heat of the liquid, 0.99; water-value of the calorimeter, 8.98 grams.

$$H = (109.7 \times .99 + 8.98)(23.12 - 21.55) \frac{32}{155} = 38,107 \text{ gram de-}$$

These experiments and others may be tabulated:—

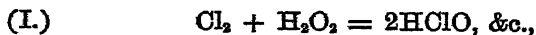
	W.	S.	V.	T° C.	° C.	M.	m.	H.
(1)	69.84	.98	8.98	24.2	21.85	.146	—	39878
(2)		."					.14	41587
(3)	109.7	.99	8.98	23.12	21.55	.155	—	38107
(4)	2021	.999	57.38	18	17.7	.48	—	41563
(5)	2020	.999	57.38	18.88	18.58	.48	—	41507
(6)	2065	.999	57.38	19.15	19	.26	—	39178

Experiment No. 6 was made in an acid liquid, but, as in Experiments 4, 5, and 6, the change of temperature is so small the results are necessarily only approximate.

It is probable that the energy due to the union of the atoms of oxygen to form the molecule, as measured in heat units, is higher than any of the values yet obtained. I shall therefore continue this study in order, if possible, to obtain nearer approximations to the energy of the oxygen molecule.

IV. HYDROGEN DIOXIDE AND CHLORINE, BROMINE, IODINE.

The reactions of chlorine, bromine, and iodine* on the dioxide also cause the evolution of oxygen. I have endeavoured to ascertain whether there is a preliminary formation of hypochlorous, hypobromous and hypoiodous acids, thus:—



analogous to—



and—



The results are, however, masked by the subsequent action of the hydrogen dioxide on these oxygen-acids (if such are really formed), oxygen being evolved, while the fact that the experiments must be

* A slight inaccuracy has crept into some of the text books (*Odling's Chemistry*, i, p. 124; *Watts's Dict.*, vol. iii, p. 198), where it is stated that iodine decomposes an equivalent quantity of hydrogen dioxide, thus:— $H_2O_2 + I_2 = 2HI + O_2$. This equation, founded on Brodie's paper on alkaline peroxides, applies strictly to the material used by him, viz., a solution of barium dioxide in acetic or other dilute acid.

conducted under such circumstances as do not admit of any reaction resembling the action of chlorine on alkaline hydrates, &c.—



adds considerably to the difficulty of the enquiry.

The action of iodine on pure dilute hydrogen dioxide is very slow, on account of the slight solubility of the iodine in the liquid. As the result of a considerable number of experiments in which iodine and the dioxide were caused to react together, first in the proportions required by the above equation (I), and secondly in other experiments where two, three, and four times the proportion of dioxide was used. I have found that in each case all the dioxide was decomposed, and that only a minute portion of the iodine remained dissolved in the liquid. The greater portion of the iodine appeared to be inert during the reaction, while the portion really active appeared to undergo repeated dissolution and precipitation. These results agree with the observations of Thénard, who states that hydriodic acid is acted on by hydrogen dioxide, iodine being set free.

The action of iodine on pure dilute hydrogen dioxide therefore resembles that of silver in being continuous, but further investigation is required to prove whether or not an oxygen compound of iodine is formed, as in the case of silver.

The presence of other substances, including neutral salts, modifies the reactions of iodine with the dioxide.

V. HYDROGEN DIOXIDE AND SULPHIDES.

The oxidizing power of hydrogen dioxide is singularly dormant in the case of *pure* sulphuretted hydrogen solution. Provided *alkaline or other salts be absent*, these two substances, hydrogen sulphide and hydrogen dioxide, may remain in contact for a considerable period with little decomposition of the sulphide beyond what takes place when its solution is kept for the same length of time. It is easy to prove the presence of either substance in the liquid after standing. By adding to a portion of the liquid very dilute chromic acid solution, and shaking up with ether the deep blue colour due to perchromic acid, shows the presence of hydrogen dioxide. Again, the precipitate of black lead sulphide obtained on addition of lead acetate solution to another portion of the liquid proves the presence of hydrogen sulphide. If, however, the latter is not in excess, the black lead sulphide in a few moments changes gradually to white lead sulphate. In this experiment there may be formed an unstable oxysulphide of lead, PbSO_2 , which is afterwards decomposed, and if so, it is suggestive of the mode of action of hydrogen persulphide on certain metallic oxides.

If in place of lead acetate we add solution of barium chloride to the mixed solution of hydrogen dioxide and hydrogen sulphide, the liquid

remains clear at first, but there is rapidly, though gradually, formed an abundant precipitate of barium sulphate.

I have also made a large number of observations on the action of the dioxide on the sulphides of the metals, of which I shall give an account in a future paper.

VI. HYDROGEN DIOXIDE AND ALCOHOL, &c.

Solutions of the dioxide of 2 to 5 per cent. have no appreciable action on alcohol of 80 per cent., nor on ether, nor on pure wood spirit.

These facts I have usefully applied in the preparation of sodium dioxide in fine crystals, this dioxide being only sparingly soluble in strong alcohol. Many double peroxides, containing two metals, may also be obtained by similar means with great facility.

(To be continued.)

II.—On Certain Bismuth Compounds. Part III.

By M. M. PATTISON MUIR, F.R.S.E.,

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1. In a former paper (this Journal [2], xv, 12) I have described four chromates of bismuth, the production of one or other of which appears to be conditioned principally by the quantity of acid or alkali present, by the temperature, and by the time during which the action is maintained. To one of the chromates described in the above quoted paper, I assigned the formula $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3 \cdot \text{H}_2\text{O}$ or $(\text{BiO})_2\text{Cr}_4\text{O}_{13}\text{H}_2\text{O}$. I have now to describe a new chromate obtained from this salt.

2. This salt was itself prepared from another chromate by treatment with strong nitric acid, heating until the whole or almost the whole of the acid was expelled, washing with water and drying. If, however, a considerable quantity of acid be allowed to remain in the salt and it be then *repeatedly* boiled with water, a light orange-coloured salt is obtained, the analysis of which, dried at 100° , gave the following results:—

(a.)	0.839	gram	gave	0.566	gram	Bi_2O_3	=	0.508	gram	Bi.
(b.)	0.3445	"		0.227	"	"	=	0.2037	"	"
(c.)	0.839	"		0.20	"	Cr_2O_3	=	0.150	"	Cr.
(d.)	0.3445	"		0.084	"	"	=	0.0575	"	"

	Calculated for $8\text{Bi}_2\text{O}_3 \cdot 7\text{CrO}_3$.	Found.				
		I.	II.	III.	IV.	Mean.
Bismuth..	59.85	60.55	59.13	—	—	59.84
Chromium	17.35	—	—	17.88	16.69	17.28

The formula given above might be written $\{\text{Bi}_2\text{O}_3 \cdot 5\text{CrO}_3\}_2\{(\text{BiO})_2$

$\text{CrO}_4\}$, as if the salt were a compound of *bismuthyl pentachromate*, and *normal bismuthyl chromate*.

3. This chromate is of a light orange colour; it is insoluble in water, but is easily dissolved by dilute mineral acids, especially by hydrochloric acid. Strong hydrochloric acid dissolves it without heating, with evolution of chlorine and formation of a very dark claret-coloured liquid. Cold caustic potash partially dissolves this chromate, and partially converts it into a loose, bulky, light-yellow salt; boiling potash converts it for the most part into a heavy, dark brown-red salt, which is insoluble in water; a portion of the chromate is at the same time dissolved with the formation of a greenish-yellow liquid. When heated, this chromate becomes much darker in colour, but the original shade is almost completely restored on cooling.

4. In Part II of these researches I have described a chromate of bismuth having the formula $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$, and prepared by boiling the precipitate obtained in a nearly neutral solution of bismuthic nitrate by means of potassium chromate, with an excess of the precipitant and a few drops of nitric acid. In attempting to prepare a fresh quantity of this salt (I had already prepared it on several distinct occasions), I found that the yellow colour of the original precipitate did not entirely give place to red, even after very prolonged heating, but that a heavy, reddish-orange-coloured salt was obtained. On account of the great density of this salt, it was extremely difficult to maintain the liquid in active ebullition: hence for the greater part of the time during which the action was proceeding the temperature of the liquid did not attain to 100° . It is very probable—as already pointed out—that temperature materially conditions the formation of these chromates of bismuth. The dense salt was washed until perfectly free from acid, dried at 100° , and analysed:—

- (a.) 0.4135 gram gave 0.275 gram Bi_2O_3 = 0.2466 gram Bi.
 (b.) 0.5095 " 0.336 " " = 0.3015 " "
 (c.) 0.4135 " 0.096 " Cr_2O_3 = 0.0657 " Cr.
 (d.) 0.5095 " 0.120 " " = 0.0822 " "
 (e.) 1.023 gram heated gently over the Bunsen lamp, lost
 0.0315 gram.

	Calculated for $5\text{Bi}_2\text{O}_3 \cdot 11\text{CrO}_3 \cdot 6\text{H}_2\text{O}$.	Found.					
		I.	II.	III.	IV.	V.	Mean.
Bismuth ..	59.15	59.63	59.17	—	—	—	59.40
Chromium. .	16.17	—	—	15.89	16.13	—	16.01
Water	3.04	—	—	—	—	3.08	3.08

The formula given above might be written $2\{\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3\} \cdot 3(\text{BiO})_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$, as if the salt were a hydrated compound of *bismuthyl tetrachromate* and *normal bismuthyl chromate*.

5. This salt appears as a finely crystalline, very dense compact powder, of a brick-red colour, inclining to orange. In its general reactions it comports itself in a manner similar to that detailed for the first chromate described. The action of hot caustic potash upon this salt appears to result in the production of the same chromate as was noticed in paragraph 3. I hope to prepare a quantity of this new chromate and to examine its properties. When heated the chromate now under consideration first becomes crimson, then brown, at which stage it is dehydrated, and is finally converted before the blowpipe into a semi-fused grey-green mass. It was found that a temperature of $210-220^{\circ}$ maintained for several hours was not sufficient to completely dehydrate this salt.

6. I will now describe some investigations lately made upon bismuth salts other than chromates.

§ 1. *Action of Chlorine on hot Bismuthous Oxide.*

This action was carried out in the hope of obtaining an oxychloride of bismuth corresponding with POCl_3 , VOCl_3 , &c., as in the lower members of the nitrogen group this appears to be the best marked oxychloride.

A quantity of pure dry bismuthous oxide was heated in a current of dry chlorine. Action began immediately, and the only product appeared to be a white crystalline sublimate, which was formed partly in the boat which had contained the trioxide, partly in the colder part of the tube. The sublimate was deliquescent, and closely resembled bismuth trichloride:—

- (a.) 0.4192 gram gave 0.306 gram Bi_2O_3 = 0.2747 gram Bi.
 (b.) 0.4192 „ 0.5425 „ AgCl and 0.006 „ Ag.

	Calculated for BiCl_3 .	Found.
Bismuth	66.35	65.53
Chlorine	33.65	32.47

This reaction is somewhat peculiar.

§ 2. *Action of Bromine on hot Bismuthous Oxide.*

7. A quantity of pure dry bismuthous oxide was gently heated for several hours along with an excess of bromine, in a long glass tube, upon the end of which a small bulb had been blown. After excess of bromine had been driven off, the product was exposed to the air for some time, and then analysed:—

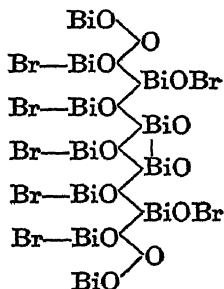
(a.)	0.5778 gram	gave	0.488 gram	Bi_2O_3	=	0.438 gram	Bi.
(b.)	0.5778	"	0.483	"	"	= 0.4335	" "
(c.)	0.5778	"	0.222	"	AgBrand	0.008	" Ag.
(d.)	0.5778	"	0.235	"	"	0.008	" "
(e.)	0.661	"	0.259	"	"	0.010	" "

Calculated for		Found.					
$\text{Bi}_{11}\text{Br}_7\text{O}_{13}$.		I.	II.	III.	IV.	V.	Mean.
Bismuth...	75.05	75.80	75.04	—	—	—	75.42
Bromine ..	18.19	—	—	17.32	18.35	17.81	17.83
Oxygen ..	6.76	—	—	—	—	—	6.75
							(by difference.)

8. The new oxybromide presents the appearance of a cream-coloured amorphous powder: it is non-deliquescent, and is unaltered by exposure to the air. When heated it slightly darkens in colour, but does not undergo decomposition; on cooling the original colour is regained.

This salt is insoluble in water, whether hot or cold; it is easily dissolved by hydrochloric or nitric acid, the addition of the latter if concentrated causing disengagement of bromine.

The formula of this oxybromide may be written as if the salt were a compound of bismuthyl bromide and bismuthous trioxide, viz., $7\text{BiOBr} \cdot 2\text{Bi}_2\text{O}_3$; or, perhaps, as an *oxybromide of bismuthyl*, $(\text{BiO})_{11}\text{Br}_7\text{O}_3$.



9. By heating together bismuthous oxide and bismuthous bromide an oxybromide is formed which I believe to be bismuthyl bromide, BiOBr .

§ 3. Action of Ammonia on Oxybromides, and on Oxide of Bismuth.

10. A quantity of the oxybromide, $\text{Bi}_8\text{Br}_6\text{O}_{15}$, described in a previous paper, was heated to dull redness in a stream of dry ammonia. The salt darkened in colour, a sublimate was produced which condensed in the colder portion of the tube in the form of a greyish-green powder, while there remained in the boat semi-fused metallic-like globules.

0.893 gram of the metallic globules gave 0.8929 gram bismuth; therefore this residue consisted of pure metallic bismuth.

11. A quantity of bismuthyl bromide, BiOBr , heated also to dull redness in dry ammonia, yielded a smaller quantity of a similar sublimate and a metallic residue, which was also shown on analysis to consist of pure bismuth:—0.5735 gram gave 0.5743 gram bismuth.

12. Bismuthous oxide, when heated to dull redness in ammonia, was also reduced to metal:—0.678 gram of residue gave 0.675 gram bismuth.

13. These reactions were carried out in the hope of obtaining a nitride of bismuth: the results were unexpected. It is probable either that a nitride was produced at a lower temperature, and was decomposed into metal and nitrogen at dull redness, or that the ammonia being decomposed into nitrogen and hydrogen, the nitrogen passed away and the phenomena noticed were the results of reduction in hydrogen. The production of water, which was noticed during the process of heating, showed that part of the ammonia, at any rate, had suffered decomposition. In order to ascertain whether a nitride was actually produced and was subsequently decomposed, a further quantity of bismuthous oxide was gently heated in dry ammonia. The salt became darker in colour, a small quantity of a yellow sublimate was produced, and a dove-brown, soft, heavy powder remained in the boat. This powder was insoluble in water, it was unacted upon by boiling caustic potash, but was readily dissolved by strong nitric acid with copious evolution of lower oxides of nitrogen.

(a.) 0.456 gram gave 0.504 gram Bi_2O_3 = 0.4523 gram Bi.

" (b.) 0.737 " " 0.816 " " = 0.7323 " "

The heavy powder was therefore metallic bismuth. Hence it appears that when bismuthous oxide is heated in dry ammonia to a temperature considerably below redness, the ammonia is partly decomposed, and the metallic oxide is reduced in the hydrogen which is thus set free, and that the nitrogen does not combine with the reduced metal. A similar reaction appears to take place in the case of the oxybromide of bismuth. I have already shown (this Journal, 1876, ii, 12) that the oxybromide, $\text{Bi}_5\text{Br}_5\text{O}_{15}$, is readily reduced when heated in hydrogen.

14. The greyish-green sublimate produced when the oxybromide, $\text{Bi}_5\text{Br}_5\text{O}_{15}$, was heated in ammonia was submitted to analysis:—

(a.) 0.53 gram gave 0.254 gram Bi_2O_3 = 0.2279 gram Bi

(b.) 0.322 " " 0.159 " " = 0.1427 " "

(c.) 0.250 " " 0.262 " AgBr and 0.01 gram Ag .

(d.) 0.5275 " boiled with KHO evolved NH_3 , sufficient to neutralise 2.5 c.c. of standard acid (1 c.c. = 0.049 gram H_2SO_4).

- (e.) 0.518 gram boiled with KHO evolved NH_3 , sufficient to neutralise 2.2 c.c. of standard acid (1 c.c. = 0.049 gram H_2SO_4).

	Calculated for $2\text{BiBr}_3 \cdot 5\text{NH}_3$.	Found.				
		I.	II.	III.	IV.	V. Mean.
Bismuth..	42.68	43.00	44.32	—	—	— 43.66
Bromine..	48.79	—	—	47.56	—	— 47.56
Ammonia..	8.53	—	—	—	8.06	7.22 7.64

15. This ammonio-bromide of bismuth is non-deliquescent, nor is it decomposed by water: it is readily dissolved by dilute acids. Strong nitric acid decomposes it with evolution of bromine. When heated, fumes of bismuth tribromide are evolved, and the salt is almost entirely volatilised, a small quantity of what appears to be the oxybromide, $\text{Bi}_3\text{Br}_6\text{O}_{15}$ remaining. A solution of this salt in hydrochloric acid, allowed to evaporate over sulphuric acid, deposited large, very pale yellow, tubular crystals. These crystals when dried by pressing between porous paper, yielded the following numbers on analysis:—

- (a.) 0.2926 gram gave 0.117 gram Bi_2O_3 = 0.105 gram Bi.
 (b.) $\left\{ \begin{array}{l} 0.2926 \text{ " " } 0.456 \text{ " } \text{AgBr and AgCl.} \\ \text{" " " } 0.294 \text{ " } \text{Ag.} \end{array} \right.$

	Calculated for $2\text{BiBr}_3 \cdot 5\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$.	Found.
Bismuth	35.43	35.82
Bromine	40.49	40.19
Chlorine	14.97	15.19

Deherain (*Compt. rend.*, liv, 724) has described a double salt analogous to this salt, viz., $2\text{BiCl}_3 \cdot 5\text{NH}_4\text{Cl}$.

When added to water this double salt is at once decomposed with the production of a milky liquid, probably containing oxychloride and oxybromide of bismuth.

16. The quantity of sublimate which was obtained when bismuthyl bromide (BiOBr) was heated in ammonia was too small to admit of much examination. It appeared to resemble the ammonio-bromide just described, and the amount of bromine found in it closely corresponded with that required by the formula $2\text{BiBr}_3 \cdot 5\text{NH}_3$, viz., 48.79 per cent.

0.295 gram gave 0.3145 gram AgBr and 0.013 gram Ag
 = 48.69 per cent. bromine.

§ 4. Preparation of Hypobismuthic Hydrate.*

17. In a former paper (this Journal [2], xiv, 149) I have described the preparation of bismuthic hydrate, $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$, by passing chlorine

through very concentrated caustic potash kept at a boiling temperature in which bismuthous oxide was suspended.

If the caustic potash be somewhat less concentrated, and the passage of chlorine be stopped when the suspended solid has been transformed into a chocolate-brown powder, and if this powder, after being washed free from alkali, be boiled for a few minutes with a little concentrated nitric acid, a reddish-yellow substance is obtained, which when washed free from acid, and dried over sulphuric acid, presents the appearance of a brownish-yellow amorphous powder. A quantity of this powder prepared as just described gave the following results on analysis :—

- (a.) 0.5805 gram gave 0.545 gram Bi_2O_3 = 0.4891 gram Bi.
 (b.) 0.657 " " 0.614 " " = 0.551 " "
 (c.) 0.352 " " 0.327 " " = 0.2935 " "
 (d.) 0.324 " " 0.302 " " = 0.271 " "
 (e.) 1.3135 " lost 0.056 after heating to 160° for some hours.

	Calculated for $\text{H}_2\text{O} \cdot \text{Bi}_2\text{O}_3$.	Found.				
		I.	II.	III.	IV.	V (mean).
Bismuth ..	83.67	84.27	83.87	83.38	83.64	83.79
Water	3.58	—	—	—	—	4.26

18. This salt to which I have given the name *hypobismuthic hydrate*, does not part with its water at 100° : when heated to 130° for two hours 3.73 per cent. of water was given off: the loss sustained at 160° (4.26 per cent.) was not increased when the temperature was raised to 190° , and maintained at that point for an hour. After heating to 190° the colour of the salt had altered to a dark-brown. The colour did not further change on raising the temperature to 230° , but decomposition began at about 250° , and on heating the salt over a Bunsen-lamp the colour rapidly became light-yellow, indicating the conversion of the bismutho-bismuthic oxide into bismuthous oxide.

Hypobismuthic hydrate is insoluble in water, whether hot or cold, it is readily dissolved by hydrochloric acid with evolution of chlorine, concentrated nitric acid very slowly dissolves this salt.

19. I attempted to prepare a potassium salt from this hydrate by boiling a quantity of it with strong caustic potash, but no action appeared to ensue, and the filtered liquid did not yield any salt containing a trace of bismuth either on evaporation or on neutralisation with acid.

Schrader (*Ann. Ch. Pharm.*, cxxi, 204) has described a hypobismuthic dihydrate, $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, obtained by a process similar to that described above.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

The Absolute Weight of Atoms. By J. ANNAHEIM (*Deut. Chem. Ges. Ber.*, ix, 1151—1152).—To show the divisibility of matter, 0·0007 gram rosaniline hydrochloride, $C_{20}H_{19}N_3\cdot HCl$ was dissolved in alcohol and the solution diluted to 1 litre. When a burette of 1 cm. diameter is filled with this solution, the red colour is clearly seen on a white background; and even if one drop be allowed to fall into a small test-tube, which is held obliquely on a white paper, the colour can still be perceived. Now, as 1 cm. of the solution gives 35 drops, it follows that 0·00000002 gram of the colour is perceptible, and on dividing this number by the molecular weight of the hydrochloride, we find that the absolute weight of 1 atom of hydrogen cannot be larger than 0·000000000059 gram.

By using a solution of cyanine, $C_{28}H_{35}N_3I$, it was found that 0·0000000285 could be seen, or that the weight of the hydrogen atom is not greater than 0·000000000054. C. S.

Specific Heats of Saline Solutions. By C. MARIIGNAC (*Ann. Chim. Phys.* [5], viii, 410—430).—This paper gives the numerical results of a long series of experiments undertaken with the view of determining whether any relation could be traced between the specific heats of saline solutions and the nature of the contained acids and bases. The results show a certain parallelism in the various series of salts; the bases, for example, often range themselves in the same order. The exceptions, however, are numerous; and calculations founded on the mean differences between the members of various series of acids and of bases, do not fairly accord with the experimental figures in more than half the number of cases. No relation was found between the specific heat and the greater or lesser tendency of the dissolved salt to form definite and crystallisable hydrates. The experiments fully confirm an observation previously made by others, as to the fact of the specific heat of a saline solution being usually less than the sum of the specific heats of the water and of the dissolved salt. In some cases, however, the inverse condition was noticed. The author admits the existence in the solution of definite and dissociated hydrates, the proportions of which vary with the quantity of water, and with the temperature; and that these changes of constitution are accompanied by a disengagement or by an absorption of heat, which diminishes or increases the apparent specific heat. R. R.

Coefficient of Expansion of Gases. By D. MENDELEJEFF and N. KAJANDER (*Deut. Chem. Ges. Ber.*, ix, 1311).—Gases having

Compression of Gases by Low Pressures. By HEMILIAN, MENDELEJEFF, and BOGUSKY (*Deut. Chem. Ges. Ber.*, ix, 1312).—Air, carbon dioxide, and sulphur dioxide, under a pressure of more than one atmosphere, are more compressible than required by Boyle's law, but less compressible under a diminished pressure; such positive deviations are shown by air between 20 and 650 mm., by carbon dioxide between 20 and 180 mm., and by sulphur dioxide between 20 and 60 mm. Hydrogen always exhibits positive deviations from the law, or contracts less than the law states. C. S.

Vapour.	Contraction at 100°.	Contraction at 180°.
Silicic chloride	2·07 per cent.	0·455 per cent.
Carbonic chloride	1·38 " "	1·367 "
Phosphorous chloride..	" " "	1·548 "

The mean coefficients of expansion, as determined from experiments at different temperatures but at the same pressure, are as follows:—

Vapour.	Mean coefficients of expansion.	
	From 100° to 125°.	From 125° to 180°.
Silicic chloride	0·00449	0·00399
Carbonic chloride	0·00470	0·00414
Phosphorous chloride	0·00489	0·00417

Migration of Gases. By F. BELLAMY (*Compt. rend.*, lxxxiii, 669—671).—The author has designated by the name of migration the passage of gases through minute channels or capillary tubes, such as exist in a bundle of cotton threads, a cotton cord, a deal shaving, &c. When a connection of this kind is made between vessels containing gases at different pressures, the gas is aspired into the vessel where

the pressure is the less. Thus, a cotton cord having one extremity passed up into a tube containing mercury inverted over the mercurial trough, and the other extremity exposed to the air, affords a conduit for the passage of air into the tube.

R. R.

Determination of Vapour-densities. By L. TROOST and P. HAUTEFVILLE (*Compt. rend.*, lxxiii, 220—223).—The authors criticise the method which some chemists have adopted of deducing the vapour-density of a substance from results obtained with mixtures of the vapour with air, or with some other inert gases or vapours. They point out that several causes of error affect these determinations, arising from the known inexactitude of Dalton's law, the departure of the vapour from the law of compressibility, and the variation of the coefficients of expansion. They animadvert upon the experiments of Wurtz for the determination of the density of pentachloride of phosphorus-vapour in mixture with the vapour of the trichloride, of which neither the coefficient of expansion, nor the law of compressibility, was accurately known.

R. R.

Determination of Vapour-densities in the Torricellian Vacuum. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, ix, 1304—1308).—Calibrated and graduated glass tubes are very liable to crack when exposed to a sudden change of temperature. The author has therefore replaced these by plain tubes, and determines the volume of vapour as follows. As soon as the mercurial column remains constant, the pendulum cathetometer is brought to a level with it, the apparatus allowed to cool, and after removing the outer glass tube the volume of vapour is marked by a strip of paper. The barometer-tube is now inverted and filled to the mark with mercury, the volume of which is ascertained by weighing it.

In the usual form of the apparatus, the whole column of mercury is not surrounded by the vapour, and therefore two corrections have to be made on reducing the height to 0°, and in so doing it is assumed that the lower part of the column has the temperature of the surrounding air, and the higher one that of the vapour, which is not correct, as the temperature of the mercury near the cork gradually changes from the lower to the higher temperature. This source of error is of little consequence if the vapour-density be taken at a low temperature, but at a high temperature it may influence the results. Wichelhaus has therefore proposed a modification of the apparatus by converting it into a syphon barometer, which allows the immersion of the whole mercurial column in the vapour. The objection to this is that only one determination at a given temperature can be made; whereas by using the common form the vapour density can be ascertained at varying temperatures. To retain the latter advantage, the barometer-tube may be surrounded by a long outer tube, which dips into the mercury, and to which at about 2—3 cm. above the level of the mercury a tube is sealed, through which the vapour escapes.

A much simpler method, however, is to retain the original form, and to rest the barometer-tube on an india-rubber plate, which is fixed on

an iron disk, to which an iron handle is attached. On the side of the plate a groove is cut, through which during the experiment the mercury can flow out. As soon as the height of the column remains constant the india-rubber plate is moved, so that the groove is removed from the opening, which is thus closed. The apparatus is now allowed to cool, and the height of the column read off at the ordinary temperature.

In the original form of the apparatus the steam is admitted at the top, and this arrangement answers very well if the boiling point of the substance does not exceed 150°. But for higher temperatures it is more convenient to allow the vapour to enter from below. For this purpose the cork of the outer tube, as well as that of the copper boiler, is provided with two holes. The tube through which the vapour enters begins just under the cork of the boiler, and ends about 4—5 cm. above the cork of the outer tube, while a second tube through which the condensed liquid flows back begins just above the cork of the outer tube, and goes down nearly to the bottom of the boiler. Thus 100—150 ccms. of aniline or any other liquid are sufficient, and if the outer tube is about 40 cm. longer than the tube, a perfectly constant temperature is obtained in 20—25 minutes by using aniline, ethyl benzoate, or amyl benzoate. The connections between the outer tube and the boiler are conveniently made of metal, and then the tube through which the vapour enters may be provided with a stop-cock, which is closed when the boiler is heated. Thus the warm liquid is forced into the space between the outer tube and barometer-tube, which is therefore gradually heated. As soon as the boiling point is nearly reached, the cock is opened to allow the vapour to enter. In this way the temperature can be kept constant for hours.

C. S.

A Method of Determining the Vapour-density of Substances boiling at High Temperatures. By VICTOR MEYER (*Deut. Chem. Ges. Ber.*, ix, 1216—1228).—The contents of this paper cannot be made intelligible in an abstract without the aid of the accompanying drawings.

J. R.

On the Separation of Mixed Liquids. By E. DUCLAUX (*Ann. Chim. Phys.* [5], vii, 264—280).—When two liquids, dissolved one in the other, are induced to separate by an external influence, such as cold, neither of the layers thereby formed consists of one of the liquids exclusively, the other being a mixture, but two new mixtures are formed in which the two substances are distributed in other proportions. At the temperature of 15—20° glacial acetic acid and benzene may be regarded as soluble in all proportions, one in the other; but when mixtures of these substances are cooled down to temperatures varying with the proportions of the constituents, separation into two layers takes place, as shown in the following statement, where the volume of the upper layer is placed above that of the lower:—

Acetic acid.

10 c.c. acetic acid	} separate at {	20.1 c.c., containing 33.3 per cent.
15 „ benzene		15° into { 4.9 „ „ 62.8 „

		Acetic acid.	
10 c.c. acetic acid	} separate at { 11° into	9.9 c.c., containing	33.6 per cent.
10 „ benzene		10.1 „ „	63.5 „
15 c.c. acetic acid	} separate at { 11° into	5 c.c., containing	35
10 „ benzene		20 „ „	62.5

A similar separation is effected by the addition to the above mixtures of a small quantity of water. Mixtures of acetic acid and petroleum also behave in the same manner.

When amyl alcohol, ethyl alcohol, and water are mixed together in such proportions that the mixture just remains homogeneous at 20°, the addition thereto of a slight excess of water causes separation into two layers having the composition shown in the following table, where the letters U and L denote the upper and lower layers:—

Amyl alcohol.	Ethyl alcohol.	Water.	$\frac{U}{L}$	Amyl alcohol		Ethyl alcohol	
				in U.	in L.	in U.	in L.
100 c.c.	100 c.c.	125 c.c.	5.8	33 p. c.	14.8 p. c.	30.6 p. e.	33.0 p. c.
100 „	110 „	152 „	2.5	33.8 „	15.6 „	30.3 „	30.9 „
100 „	133 „	220 „	0.67	30.6 „	15.2 „	29.0 „	29.2 „
100 „	150 „	260 „	0.40	31.0 „	14.4 „	29.0 „	29.0 „
100 „	166 „	292 „	0.18	33.0 „	14.8 „	—	—
100 „	200 „	400 „	0.11	35.0 „	12.0 „	26.0 „	28.0 „

The separation is effected equally by the addition of excess of amyl alcohol instead of water. Such mixtures are very sensitive also to slight changes of temperature. The following table exhibits the temperatures at which mixtures of the liquids in the proportions there given separate into two layers:—

Amyl alcohol.	Ethyl alcohol.	Water.	Temp. of separation.	$\frac{U}{L}$	Amyl alcohol	
					in U.	in L.
100 c.c.	133 c.c.	246 c.c.	30°	0.44	29.3 p. c.	16.1 p. c.
100 „	133 „	219 „	20	0.67	30.6 „	15.2 „
100 „	133 „	191 „	10	1.2	31.3 „	14.2 „
100 „	133 „	164 „	0	1.5	31.6 „	13.5 „
100 „	133 „	133 „	-14	1.8	34.4 „	10.3 „

Mixtures of methyl and amyl alcohol and water, or of amyl alcohol, acetic acid, and water, behave in exactly the same manner.

A mixture of 5 parts of alcohol of 86°, 10 parts of ether, and 6 parts of water is perfectly homogeneous; but on adding a slight excess of water ($\frac{1}{100}$) the liquid becomes turbid and separates into two nearly equal parts, both containing the three liquids. This mixture resembles, in its behaviour so far, those previously described, but it possesses the remarkable property of becoming turbid when heated. A difference of temperature of 0.1° at the critical point is sufficient to cause a sudden separation of the liquid into two layers having the

same composition as those produced by the addition of water. This property is exhibited also by a mixture of ether, acetic acid, and water.

The author recommends the employment of mixtures such as are described above for thermometric purposes. The indications of thermometers made on this principle may be rendered more apparent by adding to the liquid a drop of red ink. So long as the liquid remains homogeneous, it is uniformly coloured; but when separation takes place the colouring matter becomes concentrated in the lower layer, leaving the upper nearly colourless. Such mixtures might be used most advantageously as maximum and minimum thermometers. It is easy to prepare mixtures of amyl and ethyl alcohol and water, which will separate into two layers at any given temperature between -15° (or even lower) and 30° . The two layers, after separating, do not mix again when the temperature rises, owing to the difference in their densities. Such thermometers need be very small only, 1 c.c. of the liquid sufficing for each, so that a large number could be arranged in a small compass.

J. R.

Salt Solutions and Attached Water. By FREDERICK GUTHRIE (*Phil. Mag.* [5], i, 354—369; 446—455; and ii, 213—225).—When a solution of a salt at or a little below 0° , is further cooled, one of three things must happen, and which of them happens is determined by the strength of the solution.

1. In all solutions weaker than the cryohydrate, ice is formed at temperatures which are lower according as the solution is richer in salt.

2. In solutions of a certain strength (namely, that of the cryohydrate), combination of the salt and water takes place in definite ratio, and at a constant temperature. The solution is therefore a melted cryohydrate, and solidifies as a whole.

3. When solutions stronger than the cryohydrate are cooled below 0° , either the anhydrous salt, or some hydrate richer in salt than the cryohydrate, separates. It follows therefore that the cryohydrate is ultimately obtained, by cooling either a weaker solution, or a solution stronger than the cryohydrate, since in the one case, ice separates and the solution strengthens, while in the other case, anhydrous salt separates, and the solution becomes weakened.

It is proposed (1) to trace the history of solutions weaker than the cryohydrates, as they yield ice on cooling; and (2) to examine the separation of such anhydrous salts or hydrates, which separate when solutions richer in salt than the cryohydrates are cooled.

A solution of a salt below 0° , which is weaker than the cryohydrate, may be regarded as a solution of ice in the cryohydrate, and just as a given weight of water dissolves as a rule more of a salt the higher the temperature, so a given weight of the cryohydrate dissolves more ice at higher temperatures below 0° than at lower ones.

Again, since at any given temperature, the quantity of ice dissolved depends on the quantity of cryohydrate present, that is, on the strength of the solution, the stronger a solution is, the lower must its temperature be reduced before it can be made to yield up ice. In a similar

manner, anhydrous salt may be supposed to dissolve in the liquid cryohydrate, and to separate therefrom at 0° , or at temperatures very little below.

Solutions of various salts were prepared of known strength, by dissolving a weighed quantity of the salt in a weighed or measured quantity of water. Beginning with a 1 per cent. solution, it was cooled, the temperature noted, and the nature of the solid which separated examined. The strength of the solution was then increased regularly by 1 per cent., examined as before, and the operation continually repeated, until the solution solidified as a whole; that is, until the cryohydrate was obtained.

While the solution is weak, solidification begins, and ice separates out at moderately low temperatures, but when a certain degree of concentration is reached, the lowest temperature is obtained, and the regular cryohydrate crystallises. On continuing to increase the strength of the solution, a very slight alteration of temperature is sufficient to cause a deposit of anhydrous salt, or of some hydrate containing less water than the cryohydrate, so that, as the concentration proceeds, the temperature at which salt separates may be 40° or more above 0° ; in fact the deposition of salt has then become only a case of ordinary crystallisation.

Twenty-three complete tables are given, containing the results of examination of as many different salts; it is not, however, necessary to reproduce them here, as the only point of special interest is the temperature at which the cryohydrate forms.

The phenomenon of a solution undergoing fractional solidification by cooling may be considered physically as the homologue of the concentration of a solution by boiling. Thus:—

1. A solution weaker than the cryohydrate loses heat; ice is formed.

2. Ice continues to form, and the temperature to fall until the cryohydrate is reached.

3. Water is thus withdrawn in the form of ice.

4. At the point of saturation, ice and salt separate simultaneously, and the solid and liquid portions are identical in composition.

1. A non-saturated solution receives heat; vapour is formed.

2. Vapour forms, and the temperature rises, until saturation is reached.

3. Water is thus withdrawn in the form of vapour.

4. When the solution is saturated, vapour and salt separate simultaneously, and the same ratio exists between the vapour formed and the salt precipitated as existed previously between the water and the salt it held in solution.

Separation of Ice from Mixtures of Salts.—20 per cent. solutions of silver nitrate and ammonium nitrate were mixed together in varying proportions; also 10 per cent. solutions of ammonium nitrate and ammonium sulphate, and the temperature at which they began to give up ice was noted. This appeared to be about a mean between the glacia-

tion temperatures of the constituents. It may be calculated from the equation—

$$t = t_1 + \frac{n}{n+m} (t_2 - t_1),$$

where n = grams of A, m = grams of B of equal percentage strength, and t_1 , t_2 , the temperatures at which A and B give out ice respectively.

A few organic substances were experimented with. Cane-sugar gave a definite cryohydrate at -8.5° , but from aqueous solutions of glycerin nothing but ice could be obtained. The results with tartaric acid were rather indefinite, but, like sodium iodide, it appeared to yield two cryohydrates at different temperatures. Dry gum arabic was found to be powerless as a cryogen, and in solution it also failed to produce a crystalline compound on cooling. Albumin in form of white of egg began to separate ice at 0° , and froze into a solid mass at -0.5° . No satisfactory results were obtained by cooling solutions of gelatin, but it was noticed that a strong solution of 50 per cent. boiled steadily at 97° .

J. W.

On the Elasticity of Metals at Various Temperatures. By G. PISATI (*Gazzetta chimica italiana*, vi, 23—32).—After noticing the researches of Coulomb, Wertheim, Kupffer, and Kohlrausch and Loomis, the author describes the apparatus employed, in which the elongation of two equal portions of the same wire under various tensions and at various temperatures could be accurately measured by means of a cathetometer. On examining an iron wire which had previously been thoroughly annealed by heating it to dull redness, and allowing it to cool very slowly in this instrument, it was found that with a tension of 1800 grams, and on gradually raising the temperature to 300° , the two halves expanded very irregularly, and a similar phenomenon was observed on cooling. However, after the operation of alternate heating and cooling had been repeated several times, the wire was reduced to the *normal state*; that is the rates of expansion of the two halves of the wire coincided perfectly. The weight on one of the halves was now reduced by 1000 grams, so that one was loaded with 800, the other with 1800 grams, and the difference in elongation observed at 18.1° , and at intervals of 50° from 50° to 300° ; the length of each half of the wire when stretched by a weight of 800 grams, was 1778.22 millimeters, and its diameter, 0.4236 millimeters at 18.1° . Similar experiments were made with a steel wire, the two halves being loaded with 1000 and 4000 grams respectively, the length of each half when stretched by a weight of 1000 grams, was 1782.69 at 23.3° , and its diameter at 14.8° was 0.4940 millimeter. The results obtained in these two sets of experiments were as follows:—

Temperature.	Increase in length in millimeters.	
	Iron.	Steel.
18°	0.588	—
22	—	1.510
50	0.590	1.514
100	0.594	1.529

Temperature.	Increase in length in millimeters.	
	Iron.	Steel.
150	0.602	1.543
200	0.615	1.563
250	0.633	1.582
300	0.656	1.601

the readings giving the increase of length produced by the increased load on the one wire at the various temperatures. From the results it will be seen that the modulus of elasticity diminishes as the temperature rises up to 300° C., whilst Wertheim (*Ann. Chim. Phys.* [3], xii, 385) found that it *increased* between -15° and 200°, which is perhaps to be attributed to the latter not having brought the wire into the "normal state" previous to making measurements.

If K be the modulus of elasticity of tension, that is 10000 times the weight necessary to produce an elongation of 0.001 in a wire 1 meter long, and of section equal to 1 millimeter square—

$$K = \frac{P.L}{s.l} \quad (1)$$

where the weight P produces an elongation l in a wire whose length is L and section s . If moreover the wire be cylindrical, and at the temperature 0° have a length of L_0 , and its section a radius r_0 , its coefficient of linear expansion being α , we have—

$$K = \frac{P}{\pi r_0^2} \cdot \frac{L_0(1 + \alpha t)}{(1 + \alpha t)^2 l} = \frac{P.L_0}{\pi r_0^2 l} \cdot \frac{1}{1 + \alpha t} \quad (2),$$

which gives the modulus of elasticity at the temperature t° . Adopting Fizeau's values for the coefficient of expansion, namely—

$$\begin{aligned} \alpha &= 0.00001228 \text{ for iron,} \\ \alpha &= 0.00001112 \text{ for steel,} \end{aligned}$$

the following are the moduli of elasticity for iron and steel deduced from the author's results:—

Temperature (cor.).	Iron.	Steel.
20°	21441	18481
50	21364	18416
100	21212	18232
150	20895	18052
200	20458	17820
250	19871	17593
300	19175	17372

C. E. G.

Elasticity of Torsion. By G. PISATI (*Gazzetta chimica italiana*, vi, 57—88).—After alluding to the labours of Kupffer, Weber, and others in this subject, and to the fact that they had not examined the effects of torsion at temperatures above 100°, the author describes the apparatus employed by himself, and also gives the details of the methods. The apparatus, a figure of which is given, is very similar

to that used for the experiment on tension, but the oil-bath and the tube containing the wire is only about 0·8 met. in length; the wire for the experiment being about 0·65 met. long, and 0·25 to 0·50 mm. in diameter. The method employed was that of oscillations, measuring the number and duration of the oscillations occurring, whilst the amplitude of the oscillations gradually decreased from 90° to 10° .

In the first experiment a silver wire, 0·468 mm. in diameter, and 643·38 long, was employed, stretched by a weight of 309 grams, observations of amplitude being registered at the end of each 50 oscillations. On repeating the experiment with the same wire a second, third, fourth time, &c., it was found that the time occupied whilst the amplitude of the vibrations decreased from 90° to 10° , gradually augmented, whilst the duration of a single oscillation diminished. After the twentieth experiment, however, no further change took place (the temperature remaining constant at $26\cdot5^\circ$). From this it will be seen that a phenomenon took place similar to that observed in the experiments on tension, namely, that during the oscillations, the wire gradually underwent alteration, until finally it arrived at a normal state for the special conditions under which the experiment was made. In these experiments it was found that at first the time required to reduce the amplitude of the vibrations from 90° to 10° (nt) was $15' 22\cdot9''$; $n = 350$ being the number of oscillations in this time, and therefore the mean duration of an oscillation (t) was $2\cdot637''$, whilst, after the wire had reached the normal state these numbers were $n = 450$, $nt = 19' 42\cdot1''$, and $t = 2\cdot6269''$ respectively, so that the mean duration of a single oscillation had been diminished in the proportion $1\cdot0038 : 1$.

A fresh set of experiments was then made. The wire was heated to 100° for an hour, allowed to cool, and examined, when it was found that the time required to reduce the amplitude had again increased, whilst the duration of a single oscillation had diminished. On repeating this treatment several times, these numbers at length became constant. An oscillation observation was then taken at 100° , and also after the wire had cooled to 26° . The numbers obtained at 100° were $n = 100$, $nt = 4' 26\cdot8''$, and $t = 2\cdot668''$; and at 26° $n = 650$, $nt = 28' 09\cdot7''$, and $t = 2\cdot5995''$. On now repeating the experiment several times, the results obtained each time were found to be identical, so that the wire had reached a second normal state differing from the first normal state in the same character and in the same direction in which the latter differed from the natural state. On increasing the temperature to 200° , similar phenomena were observed, the numbers for the normal state under these conditions being:—

	n .	t .	nt .
At 200°	30	$2\cdot750''$	$1' 22\cdot5''$
Cooled to .. $25\cdot4^\circ$	1000	$2\cdot512''$	$41' 52\cdot0''$

It was then heated to 305° , cooled to 26° , and a series of oscillations observed, these operations being repeated until constant results were obtained. The numbers at $25\cdot8^\circ$ for this third normal state were $n = 1450$, $t = 2\cdot417''$ (about).

It was found, moreover, that when the wire was relieved from the

tension to which it had been subjected, even for so short a time as 30'', an alteration in the elastic state was produced, the duration and number of the vibrations being temporarily altered; but that after the wire had been caused to oscillate for a long time, stretched with different weights and at different temperatures, it was finally reduced to a normal state such that, even when the tension was varied, the same number of oscillations, n , were always observed, the temperature remaining constant.

A series of experiments was then made to ascertain the variation in the elasticity corresponding to variation of temperature, the details of which are given. Under these circumstances the number of oscillations n decreased rapidly up to 160°, and then much more slowly up to 300°, while the duration of a single oscillation gradually increased. On measuring the wire it was found to have slightly increased in length, and diminished in diameter, its dimensions now being 647·48 and 0·4661 millimeters.

Modulus of the Elasticity of Torsion at Various Temperatures.—If E is the modulus of elasticity of torsion referred to a square millimeter in section

$$E = \frac{\pi}{g} \cdot \frac{M}{t^2} \cdot \frac{L}{r^4} \quad (1)$$

where M is the moment of inertia of the tension (equal to 13608 grams per square millimeter in the experiment); t the duration of a single oscillation; L and r the length and radius of the wire; and g the acceleration of gravity expressed in millimeters. As $\frac{L}{r^4}$ varies with the temperature, if α is the coefficient of linear expansion, and T the temperature (1) becomes

$$E = \frac{\pi}{g} \cdot \frac{M}{t^2} \cdot \frac{L_0}{r_0^4} \cdot \frac{1}{(1 + \alpha T)^3}$$

where L_0 is 647·48 and r_0 0·233 millimeters, and $\alpha = 0·000·0187 + 0·000·000·010 T$.

In the following table the number of oscillations during which the amplitude was reduced from 90° to 10° is given, and also the modulus.

Temperature.	Number of oscillations.	Modulus of torsion.
0°	—	1644·5
10	—	1637·8
20	—	1630·9
30	1620	1623·8
40	1275	1616·4
50	1000	1608·6
60	780	1600·3
70	590	1591·5
80	445	1582·1
90	348	1572·0
100	277	1560·9
110	218	1548·5
120	172	1535·0

Temperature.	Number of oscillations.	Modulus of torsion.
130	135	1520.5
140	104	1502.5
150	80	1481.0
160	62	1456.0
170	48	1429.0
180	40	1400.5
190	32	1371.0
200	30	1341.2
210	28	1311.4
220	26	1281.6
230	24	1251.8
240	22	1222.0
250	20	1192.2
260	18	1162.4
270	16	1132.6
280	14	1102.8
290	12	1073.0
300	10	1043.2

Curves corresponding with these numbers and with their differences accompany the paper. C. E. G.

Retardation of Chemical Reactions by Indifferent Substances. By G. LUNGE (*Deut. Chem. Ges. Ber.*, ix, 1315—1316).—A mixture of equal volumes of fuming hydrochloric acid and glycerin (*a*) acts on ultramarine only after 45 seconds, and bleaches it in 8 minutes, while a mixture of equal volumes of water and acid (*b*) begins to act in 10 seconds and destroys the colour in 35 seconds. Mixture *a* dissolves zinc and iron much more slowly than *b*. Thus 10 c.c. of the latter dissolved 0.5 gram of nails in less than 24 hours, while *a* left after 24 hours 86.2 per cent. undissolved, and after 14 days 1.3 per cent. still remained. The cause of this is not that ferrous chloride is less soluble in glycerin than in water, because the salt readily dissolves in the former, and during the experiment none separated out. Mixtures of sulphuric acid and glycerin show a similar inactivity, and instead of glycerin gum may be used. A mixture of acid and soot scarcely acts on metals, but on removing the soot by filtration the filtrate acts like fresh acid. The retardation reaches a maximum by using a mixture of strong acid and glycerin with 5 per cent. of soot; iron nails lost in it—

	1.	2.
In 3 days	10.8 per cent.	21.2
„ 6 days	25.4 „	13.0
„ 14 days	51.0 „	—

C. S.

The Point of Combustion. By A. MITSCHERLICH (*Deut. Chem. Ges. Ber.*, ix, 1171—1178).—By this term the author understands the temperature at which a body begins to take up free oxygen. This may be a simple oxidation, or a decomposition may take place at the same

time, and the process may proceed only gradually with a slow evolution of heat or quickly with a violent evolution of heat and light.

The author describes the apparatus and the method which he used for these determinations, but these can only be understood with the help of a drawing. The results which he obtained will be published afterwards. C. S.

Contributions to the Theory of Luminous Flames. By KARL HEUMANN (*Liebig's Annalen*, 183, 1—29).—In this second contribution the author considers specially the circumstances which determine the distance existing between a luminous flame and the orifice whence it issues. His principal conclusions are as follows:—

1. The fact that a space occupied by unburned gas exists between a gas flame and the burner, or between a candle flame and the wick, as also the fact that a flame does not actually touch a cold body placed within it, is due chiefly to the cooling action of the surroundings of the flame, whereby the temperature of the gases is reduced below the ignition point.

2. The great distance existing between the flame and the burner in the case of a gas issuing under high pressure, as in the case of a gas largely diluted with indifferent gases, is to be traced partly to the cooling action already mentioned, but more especially to the fact that the rate of propagation of ignition in the neighbourhood of the burner is less than the rate at which the gaseous stream issues.

3. In order to remove other conditioning circumstances, the rate of propagation of ignition should be maintained equal to the rate at which the gas flows at that point, situated some distance from the burner, at which the flame begins. The rate of propagation of ignition will be determined, under such conditions, for many gases and vapours; and, inasmuch as this magnitude is a function of the difference between the temperatures of ignition and combustion of the combustible body, it is hoped that much light will be thrown on the relations existing between these two.

4. The rate of propagation of ignition may easily be determined for solids and liquids, and comparative quantitative expressions for the liability to ignition of combustible substances may thus be obtained.

M. M. P. M.

Inorganic Chemistry.

Production of Ozone by the Pulverization of Water. By G. BELLUCCI (*Gazzetta chimica italiana*, vi, 88—97).—Lender had noticed in the concentration of the brine springs of Kissingen by graduation, that the air in the immediate neighbourhood of the columns gave the ozone reaction, and Gorup-Besanez found that the quantity of ozone produced by the spray of water issuing under pressure was greater the more rapid the evaporation. Morin and Monte have also shown that in the pulverization of water as practised

at some thermal establishments, ozone is produced in sensible amount. These facts induced the author to make observations in the neighbourhood of the falls of Terni to ascertain if ozone was produced by the natural pulverization of the water, especially as he had often noticed the characteristic odour of ozone there. He found that Schönbein's paper was distinctly attacked in three hours, the alteration being more marked in the immediate vicinity of the falls, and especially at those seasons when the volume of water was greatest. Papers exposed at a distance from the fall within a radius of 80—100 meters were all more or less attacked, but most strongly on the banks of the stream below the fall, the current of air which invariably follows the course of a rapid stream closely shut in by rocks, or in a narrow valley, carrying along the ozone.

The author infers from these results that ozone is generally produced where water undergoes pulverization, or is converted into finely divided spray, whether this is effected by a cascade, a torrent rushing over rocks, the surf on the sea-shore, or the rolling of the waves in the open ocean. It is noteworthy that the air over the surface of the ocean is richer in ozone than that collected on the land. After discussing at length the various causes which might produce the ozone, the author arrives at the conclusion that it is due to the electrical state induced by the friction of the minute drops of water against one another, which is increased by the mineral matter suspended or even dissolved in the water. C. E. G.

Prismatic and Octohedral Sulphur. By D. GERNERZ (*Compt. rend.*, lxxxiii, 217—220).—When the contact of solid particles is prevented, fused sulphur may be indefinitely maintained in the liquid state at a temperature much below its point of fusion. Under these circumstances solidification may be induced without the introduction of a crystal of sulphur, by either rapidly cooling a part of the liquid, as by touching the exterior of the containing tube with a cold body, or rubbing the interior of the tube with a glass rod left in the liquid. In either case the sulphur solidifies at temperatures above 60° in the prismatic form, and at ordinary temperatures these prismatic crystals break up into minute octohedrons. The octohedral crystallisation may, however, be induced in the fused sulphur even at the temperature at which the prismatic occurs spontaneously as just described. This result is obtained by the introduction of an octohedral crystal, which determines a crystallisation in the octohedral form throughout the mass, but at a much slower rate than when the prismatic forms are produced. On fusing sulphur in a U-tube with proper precautions the two kinds of crystallisation can be simultaneously set up by the introduction of different crystals into each branch. R. R.

The Atomic Weight of Selenium. By O. PETTERSSON and G. EKMAN (*Deut. Chem. Ges. Ber.*, ix, 1210—1212).—The authors have attempted to arrive at the atomic weight of selenium by a variety of methods, of which two only proved practicable, namely, (1) heating silver selenite and weighing the residual silver, and (2) reducing selenious anhydride dissolved in water by means of

sulphur dioxide and weighing the precipitated selenium. The atomic weight was found to be by the first method 79.01, and by the second 79.08. The authors place more reliance on the results obtained by the second method. J. R.

Action of Halogen Acids on Selenious Oxide. By A. DITTE (*Compt. rend.*, lxxxiii, 223—225).—The compound $\text{SeO}_2 \cdot 2\text{HBr}$ energetically absorbs hydrobromic acid gas with evolution of heat, giving rise to a crystalline compound corresponding with the formula $2\text{SeO}_2 \cdot 5\text{HBr}$. This is decomposed at 65° with formation of water and disengagement of bromine, but at lower temperatures it is transformed into $\text{SeO}_2 \cdot 2\text{HBr}$ and hydrobromic acid. The following are the values of the tension of dissociation of the compound $2\text{SeO}_2 \cdot 5\text{HBr}$ at various temperatures:—

At -25°	0 mm.	At 30°	287 mm.
— 0°	108	41°	335 "
— 0°	135	54°	404 }
+ 11°	191	62°	404 } Traces of bromine
+ 14°	209	70°	Decomposition with
			abundant vapour
			of bromine.

Hydriodic acid reacts with selenious oxide even at -10° , the products being water, iodine, and selenium. Selenious oxide also combines with anhydrous hydrocyanic and hydrofluoric acids. Selenious oxide and hydroselenic acid in presence of water decompose each other with separation of selenium. This result is always the same, whether the solutions be concentrated or dilute, hot or cold; and no compound corresponding with pentathionic acid has been obtained. The reaction is a convenient means of obtaining selenium soluble in sulphide of carbon. R. R.

Action of Halogen Acids on Tellurous Oxide. By A. DITTE (*Compt. rend.*, lxxxiii, 336).—Tellurous oxide, whether crystallised or amorphous, behaves in the same manner to hydracids.

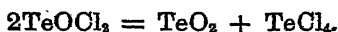
Anhydrous tellurous oxide absorbs hydrochloric acid with extrication of heat. If the vessel in which the reaction is occurring be cooled to -10° , the absorption of the hydrochloric acid ceases after a while. The substance has become light brown, and the quantity of hydrochloric acid absorbed is that which corresponds with the formula $2\text{TeO}_2 \cdot 3\text{HCl}$.

A slight elevation of temperature decomposes this compound, hydrochloric acid is evolved, and a body having the formula $\text{TeO}_2 \cdot \text{HCl}$ remains.

When this substance is heated at about 110° , drops of water appear, and are deposited on the cool parts of the vessel. These increase in quantity by increased heat; the liquid becomes darker, and at about 800° the production of the water (which should be removed as fast as it forms) ceases, and if the heat be stopped so soon as white vapours begin to appear, indicating the volatilisation of the substance left in

the vessel, this, on cooling, solidifies to a crystalline mass which consists of tellurous oxychloride, TeOCl_2 .

The oxychloride melts to a deep-coloured liquid, which, when boiled, gives off bromine-coloured vapours, and these, on condensing, deposit white crystals which consist of tellurous chloride, while a great portion of the substance is not volatile at about 400° , and consists of tellurous oxide. The oxychloride, therefore, splits up under the action of heat in the manner shown by the equation—



No compound of the formula $\text{TeO}_2 \cdot 2\text{HCl}$, analogous to the selenium compound, could be obtained. C. H. P.

Thermic Formation of Hydroxylamine or Oxyammonia. By M. BERTHELOT (*Compt. rend.*, lxxxiii, 473—478).—This paper contains a study of the thermic and chemical phenomena attending the formation and decomposition of oxyammonia, leading the author to the conclusion that this compound belongs to a special and hitherto unrecognised type, to which, among bodies already defined, the oxide of triethylphosphine offers the nearest analogy. The thermic observations confirm and specify the conditions which determine the instability of the compound. R. R.

Phosphorus Pentafluoride. By T. E. THORPE (*Liebig's Annalen*, clxxxii, 201—205).—When phosphorus pentachloride is added gradually to arsenic trifluoride (obtained by heating arsenic trioxide with fluor-spar and sulphuric acid), a violent reaction takes place, resulting in the formation of arsenic trichloride and phosphorus pentafluoride, in accordance with the equation—



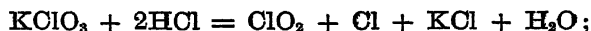
Phosphorus pentafluoride is a colourless gas, having a very pungent odour, and attacking the mucous membranes. It fumes in the air, reacting with water to form phosphoric and hydrofluoric acids. Its density was found to be 63.23, that of hydrogen being 1 (theory requires 63). Under the pressure of 12 atmospheres at 7° , it exhibits no marked deviation from Boyle's law.

The gas neither burns nor supports combustion. It is not affected by the passage of electric sparks through it when pure, nor when mixed with hydrogen or oxygen. It combines with dry ammonia to form a yellowish-white solid body, represented by the formula $2\text{PF}_5 \cdot 5\text{NH}_3$. A solution of the gas in aqueous ammonia deposits, on evaporation, crystals of ammonium phosphate ($\text{H}_2\text{NH}_4\text{PO}_4$), and ammonium and hydrogen fluoride ($\text{HF} \cdot \text{NH}_4\text{F}$). J. R.

Formation of Phosphonium Iodide. By K. LISSENKO (*Deut. Chem. Ges. Ber.*, ix, 1313).—The author believes that this compound is formed by the action of hydriodic acid on hypophosphorous acid, for when the latter is fused and saturated with hydriodic acid, a product is obtained, which, when heated in a current of carbon dioxide, yields non-inflammable hydrogen phosphide, hydriodic acid, and phos-

phonium iodide, while phosphoric acid remains behind. When 1 part of phosphorus and 2 parts of iodine are dissolved in carbon sulphide, and the latter distilled off, a red mass is obtained, which is a mixture of several compounds. On adding water, the odour of hydrogen phosphide is given off, and the solution first contains hypophosphorous acid, but on standing also phosphoric acid. The orange residue which remains appears to be solid hydrogen phosphide. C. S.

Action of Hydrochloric Acid on Potassium Chlorate. By G. SCHACKERL (*Liebig's Annalen*, clxxxii, 193—201).—Pebal showed that the action of hydrochloric acid on potassium chlorate results in the formation of chlorine and hypochloric acid (ClO_2) in varying proportions (see this Journal, 1875, 1157). The author's experiments on this subject have led to the conclusion that the action is represented primarily by the equation—



or, when sulphuric acid and potassium chloride are employed, by the equation—



but that, in most cases, there occurs a secondary action of free hydrochloric acid on the hypochloric acid first formed, whereby the proportion of chlorine is increased. The extent to which this secondary action takes place was found to depend upon the amount and strength of the hydrochloric acid present in the liquid from which the gases were evolved. Thus, when a solution of potassium chlorate was run into hot hydrochloric acid of sp. gr. 1.19, the proportion by volume of the hypochloric acid and chlorine evolved was 2 : 35.6; but when finely-triturated potassium chlorate was decomposed with hydrochloric acid diluted with twice its bulk of water, the two gases were in the proportion of 2 : 1.71. Again, when a mixture of 1 mol. of potassium chlorate and 5 mol. of potassium chloride was decomposed by sulphuric acid, the hypochloric acid and chlorine evolved were in the proportion of 2 : 5.54; but when a mixture of 4 mol. of chlorate and 1 mol. of chloride was decomposed in the same manner, the two gases were in the proportion of 2 : 1.27. Numerous other experiments were made, all leading to the same conclusion. In no case was pure chlorine obtained. The gases were analysed by Pebal's method.

J. R.

The Dissociation of the Vapour of Calomel. By H. DEBBAY (*Compt. rend.*, lxxxiii, 330).—The results of the author's experiments upon the dissociation of the vapour of calomel at 440° do not coincide with those of Odling and Erlenmeyer, according to whom the dissociation is complete, as determined from the vapour-density, and the fact that a strip of gold plunged into the vapour becomes amalgamated, and also incrustated with corrosive sublimate. This experiment with the strip of gold can only be of use, if it is established, that at 440° the tension of dissociation of the amalgam of gold is inferior to

one-half an atmosphere, which is the tension of the vapour of mercury in the mixture of equal volumes of mercury and corrosive sublimate supposed to exist by Odling's hypothesis: if it is beyond half an atmosphere, the strip of gold could not amalgamate in such a mixture; but it is shown by direct experiment that a strip of gold, heated to 440° , does not become whitened in the vapour of mercury at the ordinary atmospheric pressure; it could not, therefore, become amalgamated in the globe used for determining the vapour-density.

When calomel is heated to 440° in a platinum vessel, and a curved silver-gilt tube, through which cold water is circulating, is plunged for a few seconds into the vapour, it becomes coated with a greyish deposit, consisting of a little mercury interspersed in a powder of calomel, so fine that the mercury has not been able to attack the gold. Therefore, although calomel heated to 440° , and maintained at that temperature for some time, suffers some decomposition, it cannot be considered as established that the dissociation is complete.

C. H. P.

A New Process for the Extraction of Gallium. By LECOQ DE BOISBAUDRAN (*Compt. rend.*, lxxxiii, 636—638).—The gelatinous precipitate obtained by treating acid solutions of the gallium-bearing mineral with excess of zinc, is dissolved in hydrochloric acid; sulphuretted hydrogen is passed through the liquid; and after the gas has been expelled from the filtrate, the latter is fractionally precipitated by sodium carbonate, until gallium ceases to be thrown down, and the precipitate no longer yields the characteristic spectrum of the metal. The precipitates are dissolved in sulphuric acid, and the solution is evaporated until vapours of sulphuric acid cease to be evolved. The residue is treated with cold water, and after dilution the solution is heated to boiling, when a sub-salt of gallium is precipitated and separated by filtering while the liquid is hot. This basic salt is dissolved in a small quantity of sulphuric acid, a slight excess of caustic potash is added, and the filtrate is treated for some time with a current of carbonic acid gas, by which gallium oxide is precipitated. This is dissolved in the smallest possible quantity of sulphuric acid, a small excess of slightly acid ammonium acetate is added, and sulphuretted hydrogen is passed through the liquid, which is then filtered, diluted, and heated to boiling. The greater part of the gallium is now precipitated, and is separated by filtering the hot liquid. The precipitate is dissolved in sulphuric acid, caustic potash is added in slight excess, and the solution is filtered and submitted to electrolysis. The metallic gallium is easily separated from the platinum pole by pressing with the fingers under warm water, and the product is purified by treatment with nitric acid free from chlorine.

R. R.

On the Physical Properties of Gallium. By LECOQ DE BOISBAUDRAN (*Compt. rend.*, lxxxiii, 611—613).—The author has prepared more than half a gram of gallium; when liquid it has a silver-white lustre, but when crystallised, it shows a tinge of blue, and loses its brilliancy. Its crystalline form is octohedral. Its melting-point, averaged from six determinations, is 30.15 . It is hardly acted

on by nitric acid, diluted with its own volume of water. Its specific gravity is 5.956; when crystallised under water, it decrepitates slightly when melted. W. R.

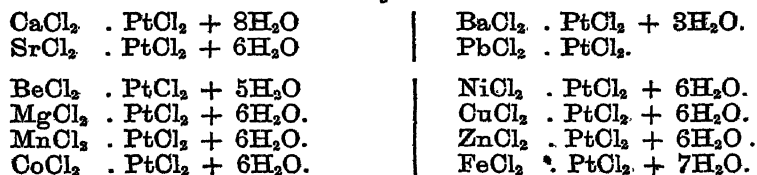
The Quantivalence of the Rare Earth-metals. By L. F. NILSON (*Deut. Chem. Ges. Ber.* ix, 1142—1148).—The author has prepared a series of chloroplatinites, of which hitherto only those of potassium, silver, ammonium, barium, and lead were known. The platinous chloride was obtained by heating chloroplatinic acid $2\text{HCl.PtCl}_4 + 6\text{H}_2\text{O}$ to 300° , washing the residue with boiling water and dissolving the residue in hydrochloric acid, which left only a small quantity of platinum behind. The chloroplatinous acid, 2HCl.PtCl_2 , still contains a few per cent. of chloroplatinic acid, which does not matter, if the chloroplatinites are less or more soluble than the corresponding chloroplatinates. In the other case the platinic chloride may be removed by sal-ammoniac or by first preparing barium chloroplatinite, and decomposing it with a sulphate. The chloroplatinites are mostly very soluble and some deliquescent, but nearly all can be obtained in large, dark red, well defined crystals.

The following is a complete list of all which are now known:—

I. *Monad Metals.*



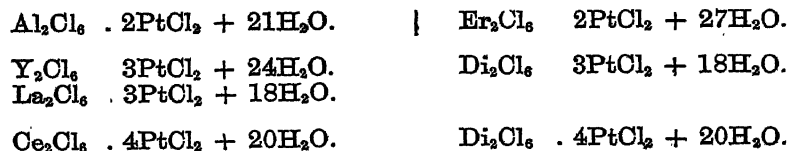
II. *Dyad Metals.*



III. *Tetrad Metals.*



IV. *Hexad Metals.*



The chloroplatinites of the monad and dyad metals are all normal salts; the mercuric salt and that of cadmium could not be obtained. The metals having a higher quantivalence form chiefly basic salts, and a few also acid salts, and it is very remarkable that in the case of the

cerite and gadolinite-metals, the normal salts crystallise only from basic and the acid salts from normal solutions. Ferric, chromic, and indium chloroplatinites could not be obtained.

The following chloroplatinates were also prepared:—

$\text{SnCl}_4 + \text{PtCl}_4 + 12\text{H}_2\text{O}$ forms glistening, thin, four-sided, yellow plates.

$\text{ZrOCl}_2 + \text{PtCl}_4 + 12\text{H}_2\text{O}$ crystallises in small, oblique, four-sided, honey-yellow plates. Cleve has already described the salt $\text{ThCl}_4 + \text{PtCl}_4 + 12\text{H}_2\text{O}$, which is further proof that thorium is a tetrad.

C. S.

The Specific Heats and Atomic Weights of Cerium, Lanthanum, and Didymium. By W. F. HILLEBRAND (*Pogg. Ann.* clxiii, 71—87).—The paper describes the method by which the author determined the specific heats of cerium, lanthanum, and didymium, operating with masses of the metals electrolytically prepared by Norton and himself. The figures obtained for the specific heats were, cerium, .04479; lanthanum, .04485; didymium, .04653. Multiplied by the hitherto-accepted atomic weights, the respective products are 4.12, 4.15, and 4.40, by which the elements would appear as exceptions to the law of Dulong and Petit. But as these atomic weights have been estimated by indirect methods based upon hypothetical assumptions, the author prepared the several oxides, and submitted them to a rigorous analysis. The results show that when, instead of CeO , LaO , and DiO , as heretofore, the formulæ of these compounds are taken as Ce_2O_3 , La_2O_3 , and Di_2O_3 , the atomic heats exhibit a satisfactory accordance with Dulong and Petit's law; for they severally become 6.18, 6.23, and 6.60. The atomic weights, as thus determined, are $\text{Ce} = 138$; $\text{La} = 139$; $\text{Di} = 144.78$.*

R. R.

New Salts of Bismuth and their Use in the Detection of Potash. By A. CARNOT (*Compt. rend.*, lxxxiii, 338).—The new salts are the double thiosulphates of bismuth and alkalis. When to a faintly acid solution of bismuth chloride, a rather strong solution of sodium thiosulphate is added, the liquid becomes yellow, but remains clear; water may then be added in any quantity without producing any alteration, if the amount of thiosulphate, which should be about three times as much as the bismuth, is sufficient. This double salt with sodium is also soluble in alcohol. The aqueous solution decomposes on standing, the more rapidly in proportion to its concentration; heat also assists the decomposition, the double salt splitting up into bismuth sulphide and sulphuric acid.

Potassium chloride added to an alcoholic solution of the sodium

* Mendelejeff, from considerations deduced from the "periodic law" of the elements, likewise regards the oxides of cerium and didymium as sesquioxides, R_2O_3 , assigning to both these metals the atomic weight 138. He has also made a determination of the specific heat of cerium, for which he finds the number 0.050, agreeing nearly with that found by Hillebrand. On the other hand, he regards lanthanum oxide as LaO_2 , and estimates the atomic weight of lanthanum at 180. (See this Journal, vol. xxvi, p. 1004.)—[Ed.]

salt affords a yellow precipitate, which rapidly coheres on agitation. The reaction succeeds equally well with a mixture of potassium chloride and nitrate, but not with sulphate. No precipitate is formed by the chlorides of ammonium and the ordinary metals which are not precipitated by sulphuretted hydrogen, but the chlorides of barium and strontium afford a white precipitate in either aqueous or alcoholic solutions of the double salt. The potassium precipitate is soluble in water, but nearly insoluble in alcohol; it keeps well when dry, but rapidly alters when moist, particularly when in contact with the mother-liquors, which themselves soon decompose, bismuth sulphide being in all cases deposited.

The composition of the potassium salt is expressed by the formula $\text{Bi}_2\text{O}_3 \cdot 3\text{S}_2\text{O}_3 + 3\text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$. It is crystalline, the crystals being the more marked in proportion as they are more slowly produced. Some very good crystals were obtained by redissolving in water some of the precipitated salt (after filtering off the mother-liquors), and adding alcohol till precipitation was on the point of occurring, and then plunging into the solution a dialyser containing strong alcohol. As the alcohol diffused, the salt slowly crystallised out, chiefly on the membrane of the dialyser. These crystals keep in the air without alteration.

C. H. P.

Researches on the Solution of Gases in Iron, Steel, and Manganese. By L. TROOST and P. HAUTEFEUILLE (*Ann. Chim. Phys.* [5], vii, 155—177).—This is a reprint of several papers which have appeared in the *Comptes rendus de l'Académie des Sciences*, and in abstract in this Journal (1873, 729; 1875, 610 and 790). Appended is the following summary of the general results arrived at:—

1. Whenever cast iron is kept in fusion in contact with silica or silicates, it evolves carbon oxide resulting from the action of iron carbide on silica; the iron, consequently, becoming poorer in carbon and richer in silicon.

2. Melted cast iron dissolves considerable quantities of hydrogen, the solubility of the gas being diminished by the presence of silicon and much increased by the presence of manganese.

3. Carbon oxide is much less soluble than hydrogen in the different varieties of cast iron. Its solubility is diminished or even annulled by the presence of manganese.

4. Pig iron, after cooling, retains gases which may be extracted by heating the metal to a temperature not exceeding 800°. Hydrogen is always more abundant than carbon oxide, both in the solid and the fused metal, and is more persistently retained by the metal. Manganiferous iron retains more hydrogen than does ordinary cast iron.

5. Steel dissolves less gas than cast iron, hydrogen predominating over carbon oxide, and being more forcibly retained by the metal.

6. Soft iron, on the contrary, dissolves more carbon oxide than hydrogen, and retains it more forcibly.

7. Finely-divided pure iron, deprived of gases, decomposes water slowly at the ordinary temperature, and rapidly at 100°, the decomposition being more rapid the finer the state of division of the iron.

J. R.

Salts formed by Manganese Peroxide. By E. FREMY (*Compt. rend.*, lxxxii, 1231—1237).—Manganese peroxide in the anhydrous state is very commonly considered as an indifferent oxide; sometimes, however, it behaves like a saline oxide, and less frequently as a metallic acid; in the present instance the author wishes to show that it is also capable of functioning as a true base.

He has succeeded in combining the peroxide with sulphuric acid by acting directly on the hydrate $\text{MnO}_2 \cdot 2\text{H}_2\text{O}$; but the best method of operating seems to consist in decomposing potassium permanganate with a considerable excess of sulphuric acid. 100 grams of permanganate are treated with a cold mixture of 500 grams of sulphuric acid and 150 grams of water, whereupon an oily layer of permanganic acid separates, which gradually decomposing forms, at the end of a few days, a deep yellow liquid, from which crystals can be obtained.

This salt the author first regarded as a sulphate of the sesquioxide, but the following considerations induced him to alter his opinion, and to look upon it as a salt of the peroxide. It is deliquescent, soluble in sulphuric acid, and decomposed by water, forming at the same time a hydrate of the peroxide, $\text{MnO}_2 \cdot 2\text{H}_2\text{O}$. The liquor resulting from this decomposition contains no manganese.

The yellow liquor exposed to the air or saturated with potassium sulphate deposits a black subsulphate, of the composition $\text{MnO}_2 \cdot \text{SO}_3$, which when redissolved in sulphuric acid, reproduces the yellow sulphate.

Certain salts such as manganous sulphate, potassium sulphate, &c., combine with the yellow sulphate and form well-crystallised double salts.

The analysis of the new compound was effected by making it react upon an acidulated solution of ferrous chloride of known strength, and then titrating the residual iron by means of a solution of permanganate.

	Experiment.	Theory.
Manganese.....	63.62	63.28
Oxygen	37.00	36.72

Five new compounds have been prepared from the yellow liquid before mentioned: an amorphous hydrate; a crystalline hydrate; two subsulphates; and a double sulphate containing both protoxide and peroxide of manganese: the analyses of this latter salt led to the formula $\text{MnO}_2(\text{SO}_3)_2 \cdot \text{MnO}(\text{SO}_3) \cdot 9\text{H}_2\text{O}$. This double salt may be produced by the careful addition of reducing agents, such as alcohol, to the solution of the yellow sulphate; it is of a rose colour and easily decomposed by water.

It is possible, of course, to regard this compound as containing manganese sesquioxide, but the existence of a corresponding potassium salt, and the fact that when decomposed by an alkali, it gives a precipitate which yields a quantity of manganous oxide to ammonia, leaving a residue of peroxide, are sufficient to show that the manganese exists in the salt in two different states of oxidation. Manganese sesquioxide does not break up under the action of ammonia.

Manganese peroxide does not appear to be the only oxide of the

formula RO_2 which can unite with acids to form salts, inasmuch as the author has obtained several definite combinations of stannic oxide, SnO_2 , with sulphuric, nitric, and hydrochloric acids. J. W.

Mineralogical Chemistry.

Mineralogical and Crystallographical Notices (continued).
By A. VON LASAULX (*Jahrb. f. Min.*, 1876, 353—368).—*Aërinite*, a new mineral, is characterised by its intense and brilliant colour, varying from dark-blue to light sky-blue. It possesses a dense, indistinctly fibrous, foliated structure, being at the same time of a thoroughly earthy nature, a crystalline structure being scarcely discernible. A thin section still exhibited a deep blue colour, and was distinctly pleochromatic, the colours varying from dark sky-blue, light-blue to yellowish-blue. In polarised light the section appeared almost uniformly of a dark-green colour, thus differing from lazurite, which still retains its blue colour in polarised light. The crystal-system is probably either rhombic or clinorhombic. Hardness 3 to 4; some parts can be scratched with the finger-nail, others only with a knife. Streak-light bluish-grey. Binds together before the blowpipe, forming eventually a grey blistered slag containing here and there small metallic magnetic grains, proving the presence of iron. Acids attack the mineral easily in the cold, quickly removing the blue colour and causing a deposition of powdery silica. From these reactions it is evident that the mineral is neither vivianite, crocydolite, nor lazulite. A portion of the mineral was fused with sodium carbonate and analysed, when its percentage composition was ascertained to be as follows:—

SiO_2 .	Al_2O_3 .	Fe_2O_3 & FeO .	Mn_2O_3 .	CaO .	MgO .	H_2O .
48.528	7.551	32.785	1.167	3.586	0.900	6.158 = 100.675

A previous spectroscopic examination had proved the absence of alkalis. It is evident that the mineral must be a hydrated ferrosio-ferric silicate (ferric oxide predominating), belonging either to the same class of minerals as gillingite, or to the chloropals. Specific gravity 3.0185. From a microscopical examination the author observed that aërinite is the cement or binding material of a great mass of what are apparently cleavage-pieces of quartz, olivine, felspar, and augite, which are regularly embedded in it, sometimes in clumps and round masses, and occasionally separated by broad zones of the blue mineral. The quartz occupies only a secondary position, exhibiting at times, however, a hexagonal section, and containing very large fluid enclosures which are moveable. The felspar is often observed slightly decomposed into serpentine. From the manner in which the particles of olivine occur in aërinite, the author considers it highly probable that the latter is a secondary product from the former, as portions of olivine which are near one another but separated by aërinite, possess uniform polarisation, thus showing that they all probably belonged to

the same individual originally. Magnetite also occurs in the mass with apatite, which is often intergrown with quartz and plagioclase. Hollow spaces are observed, not only in the aerinite, but also in the embedded minerals, sometimes containing a finely fibrous, radiating, zeolitic mineral. This zeolitic mineral appears to exert some influence upon the colour of the aerinite, as the latter has a leek-green colour at the points of contact with it.

Pilinite, a new mineral, occurs in hollows in the granite of Striegau, as a felt-like formation of extraordinarily fine, colourless, or white flexible needles. The straight needles never exceed 0.01 mm. in breadth, and have a tabular appearance, owing to the predominance of two faces in the zone of prismatic development, indications of other faces in this zone being very rare. Indistinct sections appeared to be elongated rhombs. A very distinct cleavage was observed at right angles to the direction of prismatic development, no doubt being a basal cleavage, as all the larger prisms are closed by this cleavage face; in addition to the basal cleavage there is also a less complete prismatic cleavage. Examined in polarised light the mineral proved to be double refractive, the principal directions of vibration being parallel to, and at right angles to the vertical axis, or coincident with the cleavage directions. Total darkness was observed when the edges of a cleavage plane (a long prismatic edge and a short basal edge) are parallel with the "chief section" of one of the crossed Nicol's prisms. Extremely small rhombic sections were obtained and measured (approximately), and found to have angles of 120° and 60° : and from the other optical properties of the mineral von Lasaulx concludes that it crystallises in the rhombic system. It melts very easily in the flame of a Bunsen lamp, with intumescence, becoming eventually a transparent and nearly colourless glass. In the matrix it gives off water. An analysis showed it to have the following composition:—

SiO ₂ .	<u>Al₂O₃.Fe₂O₃.</u>	CaO.	Li ₂ O.	<u>MgO.Na₂O.K₂O.</u>	H ₂ O.
55.70	18.64	19.51	1.18	traces.	4.97=100.00

Specific gravity at $15^\circ \text{C} = 2.263$. From the analysis the formula $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{Li}_2\text{O} + 2\text{H}_2\text{O}$ is obtained, which does not agree with the formula of any known zeolite, unless it is supposed that the sodium oxide of analcime is replaced by calcium oxide, when it would nearly agree with the formula for that mineral, but against this is interposed the crystallographic system of the new mineral. The author prefers to give it a distinct name, as it does not agree with any known mineral species. The genesis of pilinite stands in direct connection with the occurrence of calcite in the hollows of the Striegau granite.

Note on Ardennite.—A small brownish-yellow transparent crystal of this mineral was characterised by the predominance of the macrodome $\overline{\text{P}}_{00}$, which was easily measured, and the angle found to be $112^\circ 15'$, thus agreeing very closely with the angle calculated by vom Rath, viz., 112.12° . The angle of the prism was ascertained by measuring over the macropinacoid $\alpha\overline{\text{P}}_{00}$, and found to be $130^\circ 20'$, the angle calculated by vom Rath being $130^\circ 0'$. The faces of a brachydome, which could not be measured, were observed on one crystal, whilst

another crystal nearly two inches in length and three lines in breadth, was strongly vertically striated on coP and coPoo . At the same time the macrodome (which was partially attached to quartz) was strongly striated parallel to the combination-edges with the pyramid. The prism of this crystal was much bent and evenly broken through at right angles to the vertical axis, thus adding a basal cleavage to the other three cleavage directions already described (*Pogg. Ann.*, 149, 241; *Jahrb. f. Min.*, 1872, 930). Impressions of the striation are observed on the quartz, similar to those observed with tourmaline and microscopical apatite; from this fact it may be safely inferred that ardennite is the primary formation. Pisani stated that ardennite always contained arsenic, but the author has repeated the analysis of the specimen first described by him (*Jahrb. f. Min.*, 1874, 276), and confirms his statement that it was free from arsenic. Since then an improved method of separating vanadic acid in presence of alumina, discovered by Dr. Bettendorff, has enabled the author thoroughly to examine this mineral, and as the result of the analyses it appears that there are two varieties of ardennite, viz., (1) arsenic-ardennite; (2) vanadium-ardennite, the first having a very pale sulphur-yellow colour, and the second a colophonium-brown colour, the colour becoming darker as the percentage of vanadic acid increases, and lighter as the percentage of arsenic acid increases.

Bettendorff separates vanadic acid from alumina by precipitating them from their solution with ammonia as vanadate of aluminium, an excess of ammonia having no influence. The precipitate is then digested with ammonium phosphate on a water-bath, when the yellow precipitate becomes white, a double decomposition having taken place, viz., aluminium phosphate remains insoluble and ammonium vanadate is in solution. Ferric oxide does not interfere with this reaction.

Two analyses were made of (1) light coloured ardennite; and (2) colophonium-brown ardennite, resulting as follows:—

	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	CuO	VO_5	AsO_5	H_2O
No. 1..	27.50	22.76	1.15	30.61	1.83	1.38	0.17	0.53	9.33	5.13=100.39
No. 2..	27.84	24.22		26.70	2.17	3.01	—	9.20	2.76	5.01=100.91

It is found that the percentage amounts of vanadic acid and arsenic acid vary considerably, showing that they replace each other vicariously. Some of the arsenic-ardennites appear to have a dark colour, but it is owing to an outward film of earthy pyrolusite, which is easily removed by hydrochloric acid. The primary ardennite is undoubtedly vanadium-ardennite, as it is always perfectly clear and transparent, whilst the lighter arsenic-ardennite is completely opaque, and appears rather porous, thus favouring the assumption that it is a secondary product of the decomposition of vanadium-ardennite. C. A. B.

Analysis of Chrysocolla and Copper-pitchblende. By HUTCHINGS (*Chem. News.*, xxxiv, 141).—The minerals are from Mexico, and are imported into England in large quantities for copper smelting. The chrysocolla has a light bluish-green colour; hardness, 4.0. The copper-pitchblende is dark brown, almost black;

hardness, 6·0. It contains large quantities of gypsum intermixed, and here and there copper carbonates. When large lumps are broken open, they often show drusy cavities in which the chrysocolla occurs botryoidal. This botryoidal chrysocolla is always coated over with a thin layer of quartz, sometimes amorphous, but more frequently beautifully crystallised in very minute crystals. The minerals were very pure, and were dried at 95° for some hours previous to analysis :—

	Chrysocolla.	Copper-pitchblende.
Silica soluble in Na_2CO_3 ..	62·42	20·63
Silica insoluble in Na_2CO_3 ..	3·83	7·35
Copper oxide	25·69	28·59
Lead oxide	0·12	0·41
Ferric oxide	0·26	10·94
Alumina	—	0·15
Manganous oxide.....	trace	17·53 }
Oxygen	—	8·60 }
Cobalt oxide.....	trace	0·35
Zinc oxide.....	0·34	1·54
Lime	0·74	0·92
Magnesia	1·06	—
Water	6·13	8·30
	100·59	100·31

D. B.

A Lithia-bearing Variety of Biotite. By G. W. HAWES (*Am. J. of Sci.* [3], xi, 431).—This mineral is from felspar quarries in the large granite veins near Portland and Middletown in Connecticut. It is black and lustrous, but in thin plates transparent brown and uniaxial. Specific gravity 2·96. Results of analysis :—Silica, 35·61; alumina, 20·03; ferric oxide, 0·13; ferrous oxide, 21·85; manganous oxide, 1·19; magnesia, 5·23; potash, 9·69; soda, 0·52; lithia, 0·93; titanatic acid, 1·46; fluorine, 0·76; water, 1·87, with a trace of chlorine. The ratio of R : R : Si is 1 : 1 : 2; and thus the analysis shows that this mica is an iron biotite in which lithia replaces part of the potash.

R. R.

Note on a New Cornish Mineral. By FREDERICK FIELD (*Chem. News*, xxxiv, 147).—This mineral has the formula $3\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$; it is green transparent, and crystallises in rhombs; dissolves in hydrochloric acid, and loses water and turns black when heated *per se*. Hardness, 3·5.

W. R.

A Sulphantimonide of Lead found at Arnsberg, Westphalia. By F. PISANI (*Compt. rend.*, xxxiii, 747—749).—The mineral examined by the author was of a steel-grey colour and carious structure, with cavities filled with crystals. Hardness, 2·5; density, 5·73. Examination and analysis showed it to be a true crystallised heteromorphite.

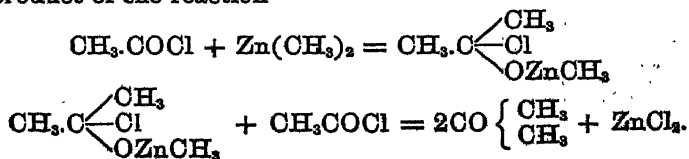
R. R.

Origin of Crystalline Rocks. By A. M. LÉVY (*Compt. rend.*, lxxxiii, 749—752).—The results of a microscopic examination—which the paper describes—of certain petrosiliceous rocks, invalidate, in the author's opinion, the theory which regards crystalline rocks as formed from vitreous rocks by a process of devitrification. R. R.

Experiments and Observations on Vitreous Rocks. By STAN. MEUNIER (*Compt. rend.*, lxxxiii, 616—619).—As each group of vitreous rocks resembles in composition a group of crystalline rocks, they might be supposed to be simply fused crystalline rocks; but this supposition cannot be maintained on careful examination, for they are found to contain water and other volatile substances. Various facts, one of which is the existence of spherulitic obsidian, lead to the supposition of a true devitrification. The author experimented on small fragments of obsidian, in order to discover if, by application of heat, they would become devitrified, and found that when heated for eight days to a temperature below their fusing point, some samples remained practically unaltered, while in others white grains of felspar and prisms of augite were developed. These crystals were probably present before application of heat. It is probable, therefore, that devitrification does not take place in obsidian and gallasite below their point of fusion. Even in a pasty condition, as shown by another series of experiments, these rocks are not devitrified. Nevertheless, when they were fused for 36 or 48 hours, and then exposed for eight days to a temperature favourable to devitrification, some particles which acted on polarised light were observed, showing a commencement of crystallisation. In some cases the angles of fracture were rectangular or hexagonal, analagous to those of felspars. On analysis their composition was found to resemble that of orthose. The conclusions at which the author has arrived are: that vitreous rocks are not a product of fusion of crystalline rocks, but that crystalline rocks are derived from vitreous rocks by devitrification; that obsidian and allied rocks cannot be directly devitrified, owing to the escape of gas bubbles, but that this devitrification takes place after they have been fused so as to expel all volatile matter. W. R.

Organic Chemistry.

Formation of Tertiary Alcohols. By D. PAWLOW (*Deut. Chem. Ges. Ber.*, ix, 1311).—In the formation of these alcohols 2 mol. of the zinc-compound act on 1 mol. of the acid chloride. At the same time condensation-products of acetones are formed, because the latter are also a product of the reaction—



The acetone is then further acted upon by the zinc methide, for on adding the latter body to acetone, mesityl oxide is formed, while among the products of the action of zinc methide on propionyl chloride, the oxide $C_8H_{14}O$ boiling at $167-168^\circ$ could be isolated.

Ethylisopropyl ketone boils at $117-119^\circ$, and is oxidised to acetone and propionic acid.

By acting on butyryl chloride with zinc methide and ethide, the tertiary alcohol $C_8H_{17}(OH)(C_2H_5)COH$ was obtained, which boils at $135-138^\circ$, and yields a heptylene boiling at $90-95^\circ$. Methyl-ethylisopropyl carbinol, which was obtained by an analogous reaction, boils at $124-127^\circ$, and its heptylene at $75-80^\circ$. C. S.

Conversion of Acid Chlorides into Alcohols. By D. DJAKONOW (*Deut. Chem. Ges. Ber.*, ix, 1312).—A better yield is obtained by employing sodium instead of its amalgam, which Saytzeff used.

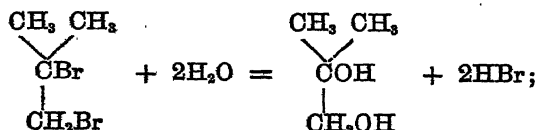
C. S.

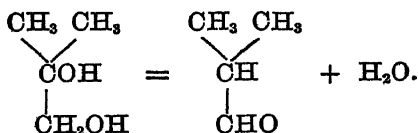
Cholesterin. By W. E. WALITZKY (*Deut. Chem. Ges. Ber.*, ix, 1310).—Cholesterin from brain yields the chloride $C_{26}H_{43}Cl$. This chloride was heated with the acetates of potassium, sodium, and silver in presence of alcohol or acetic acid under varying conditions, but Berthelot's acetate was not formed, the chloride remaining either unchanged or losing chlorine and being converted into a resin. Alkalis, sodium sulphite, potassium cyanate and cyanide, mercuric cyanide and silver cyanide, gave similar results. When the chloride is heated with sodium ethylate, the hydrocarbon $C_{26}H_{42}$ is formed, which is sparingly soluble in alcohol, more readily in ether, and crystallises in transparent needles melting at 80° . On heating the chloride with alcoholic ammonia, a resin is formed together with the compound $(C_{26}H_{42})_2HCl$. The iodides of potassium and aluminium do not convert the chloride into an iodide, and aniline does not act on it, whereas when sodium amalgam is added to its boiling alcoholic solution, the hydrocarbon $C_{26}H_{44}$ is formed, crystallising from ether-alcohol in large pointed pyramids, melting at about 90° . Aqueous hydriodic acid and iodine and phosphorus convert cholesterin into impure $C_{26}H_{42}$.

According to Latschinoff, cholesterin yields with potassium permanganate the acid $C_{26}H_{42}O_7$, which forms amorphous salts; only those of the alkalis are soluble in water, the others are insoluble in water, alcohol, and ether, but dissolve in benzene.

C. S.

Action of Water on Glycols, By M. NEVOLÉ (*Compt. rend.*, lxxxiii, 228—229).—Bromide of isobutylene, when heated with water in a sealed tube, is transformed into the corresponding aldehyde. The author explains this reaction by supposing that the glycol is first formed, and then changed into aldehyde by elimination of the elements of water, thus:—





For he found that when the glycol prepared from bromide of isobutylene was heated with water for some hours at 200° , isobutyric aldehyde was in fact formed. The parallel reaction took place with ethylenic glycol at a somewhat higher temperature.

R. R.

Preparation of Trimethylene Bromide. By J. LERMONTOFF (*Liebig's Annalen*, clxxxii, 358—362).—The author prepares this substance as follows:—Allyl bromide is saturated at -10° to -15° with dry hydrogen bromide, and afterwards heated to 165 — 170° in the same vessel for 24 hours. Nearly the whole of the product boiling at high temperatures is trimethylene bromide. About one-third of the allyl bromide remains unaltered after this operation, but if the liquid be again saturated with hydrogen bromide and heated for 24 hours, the whole enters into combination. The product is purified by distillation with steam.

J. R.

Preparation of Dichloroacetic Acid. By O. WALLACH (*Deut. Chem. Ges. Ber.*, ix, 1212).—This substance may be prepared as follows:—Ethyl dichloroacetate (obtained by the action of potassium cyanide on alcoholic chloral) is dissolved in alcohol and mixed with an equal number of molecules of potash. The crystals of sodium dichloroacetate thereby produced are dried, placed in a long combustion tube, and submitted to the action of a current of hydrogen chloride so long as the gas is absorbed. The dichloroacetic acid resulting from this operation is then distilled off in a slow stream of hydrogen chloride. The acid boils at 189 — 191° , solidifies at 0° , and yields a crystalline potassium salt.

J. R.

Action of Potash on Trichlorobutyric Acid. By K. GARZAROLLI-THURNLAK (*Deut. Chem. Ges. Ber.*, ix, 1209).—The author has obtained by this reaction an acid having the same composition as Gottlieb's dichlorocrotonic acid, but differing therefrom in properties. The investigation is not yet complete.

J. R.

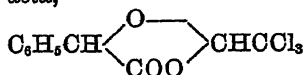
A Simple Method of preparing Glycollic Acid. By RUDOLPH FITTIG (*Deut. Chem. Ges. Ber.*, ix, 1198).—When chloroacetic acid in moderately strong aqueous solution is boiled for a few hours, it is almost completely converted into glycollic and hydrochloric acids. On distilling the product and evaporating the residue over the water-bath there remains a syrupy liquid containing only a trace of chlorine, from which it may be freed by again evaporating with water. The calcium salt obtained from the residue is pure glycolate.

J. R.

Action of Chloral and Bromal on Oxy-acids. By O. WALLACH

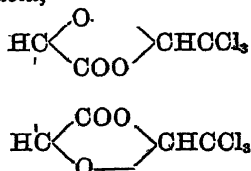
LACH (*Deut. Chem. Ges. Ber.*, ix, 1214—1216).—The following bodies are obtained by heating chloral with the respective acids:—

Chloralide of mandelic acid,



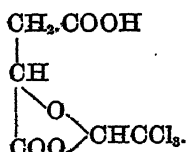
Snow-white crystals melting at 59°, boiling at 305—310° with partial decomposition, soluble in alcohol and ether, insoluble in water.

Chloralide of tartaric acid,



Small crystals, melting at 122—124°, insoluble in water, soluble in warm alcohol and ether.

Chloralide of malic acid,



A monobasic acid, forming fine crystals which melt at 137° and dissolve freely in hot water.

The corresponding *bromalides* are obtained by precisely similar reactions. J. R.

Synthesis of α -Oxybutyric Acid. By S. PRSCHIBITESK (*Deut. Chem. Ges. Ber.*, ix, 1312).—This acid is formed by the action of hydrocyanic and hydrochloric acids on propionic aldehyde. C. S.

Action of Allyl Iodide and Zinc on Ethyl Oxalate. By E. PATERNO and P. SPICA (*Gazzetta chimica italiana* vi, 38—39).—On gently heating a mixture of one molecular weight of ethyl oxalate and 4 of allyl iodide with granulated zinc, an energetic action is set up, which must be moderated by affusion of cold water. On adding water to the product and distilling, an oil passes over, which when subjected to fractionation, may be separated into allyl iodide and a compound boiling at 207—209°. This by analysis gave numbers corresponding with the formula $\text{C}_{10}\text{H}_{18}\text{O}_3$, so that there can be no doubt the substance is ethyl-diallyloxalate, $\text{HO.C}(\text{C}_3\text{H}_5)_2\text{CO}(\text{OC}_2\text{H}_5)$. From this ether the acid may be obtained by saponification, but the authors have not yet examined it. They thought it probable that the acid $\text{C}_8\text{H}_{10}\text{O}_2$ might be obtained by Frankland and Duppa's method of treating the ether with phosphorus trichloride, but the results were unsatisfactory. C. E. G.

On so-called Non-saturated Compounds. By RUDOLPH FITTIG (*Deut. Chem. Ges. Ber.*, ix, 1191—1195).—This is a continuation of a previous paper on the same subject, of which an abstract has already appeared in this Journal (1876, i, 897).

It was stated before that *maleic acid* and its *anhydride*, when dissolved in fuming hydrobromic acid, are converted into fumaric acid. Further examination of this reaction has shown that monobromosuccinic acid is formed at the same time. The two products are formed in about equal numbers of molecules, whatever the proportion of hydrobromic acid employed.

Fumaric acid, when heated to 100° with a sufficiently large excess of hydrobromic acid, is rapidly and completely converted into monobromosuccinic acid, identical with that obtained from maleic acid. A strong solution of monobromosuccinic acid, prepared in the cold, is almost completely decomposed by boiling for a few hours, the product being pure fumaric acid.

Citraconic acid and its *anhydride* dissolve in fuming hydrobromic acid to a clear liquid, which in the course of a few days deposits small hard crystals of bromopyrotartaric acid. This acid, when recrystallised from hot water, forms large transparent monoclinic crystals melting at 148° with decomposition. It is resolved by prolonged boiling with water into methacrylic and hydrobromic acids and carbon dioxide, and the same decomposition is brought about instantaneously by dissolving the acid in excess of sodium carbonate and heating the solution to the boiling point. The reaction affords a satisfactory means of preparing methacrylic acid.

Itaconic acid dissolves in fuming hydrobromic acid, and forms with it a crystalline addition-product melting at 137°, which is still under investigation.

Crotonic and *isocrotonic acids* dissolve in hydrobromic and hydriodic acids, forming solutions which deposit substituted bromobutyric acids after standing a few days. These products are completely converted into normal butyric acid by treatment with sodium-amalgam.

Cinnamic acid combines with hydrobromic and hydriodic acids in the cold. Bromohydrocinnamic and iodhydrocinnamic acids both form pearly laminæ, the former melting at 128°, and the latter at 120°, with decomposition.

J. R.

On the Isomeric Pyrotartaric Acids. By W. MARKOWNIKOFF (*Liebig's Annalen*, clxxxii, 324—346).—The author's investigation of these acids has led to the following results:—

1. *Pyrotartaric Acid from Propylene Bromide*.—This acid was prepared by heating to 150° a mixture of propylene bromide with excess of potassium cyanide and alcohol, and afterwards heating the propylene cyanide thus formed to 100° with fuming hydrochloric acid. The product, when purified by crystallisation, melted at 112°.

The neutral *ammonium salt* forms crystals very easily soluble in water and sparingly soluble in alcohol.

The *calcium salt* forms small prismatic crystals.

The acid, when heated to 200°, gives off water and is converted into the anhydride, $C_4H_2O_3$, which is a colourless oily liquid boiling at

244.9° (corr.), tasting sweet and sour, and combining but slowly with water. Pyrotartaric acid prepared from tartaric acid behaves in the same manner, so that the two acids are identical.

2. *Isopyrotartaric Acid from α -Bromobutyric Acid.*—This acid, termed by the author α -isopyrotartaric acid, was prepared by acting on ethyl bromobutyrate diluted with alcohol with potassium and mercury cyanide at 130°, and heating the ethyl cyanobutyrate thus formed to 100° with hydrochloric acid. It crystallises when pure in rhombic prisms, which melt at 111.5° and dissolve easily in water, alcohol, and ether. At 160° it begins to decompose into carbon dioxide and butyric acid.

The *potassium salt* forms small crystals easily soluble in water, insoluble in alcohol.

The *sodium salt* crystallises in granular masses, more freely soluble in cold than in hot water.

The *silver salt* dissolves sparingly in boiling water. It does not blacken at 100°.

The *zinc salt*, formed by saturating the acid with zinc carbonate, is sparingly soluble in cold and hot water. At 150° it begins to decompose into butyric acid, carbon dioxide, and water.

The *lead salt* is a heavy white precipitate, which is not affected by boiling.

The *ethyl-ether* of this acid, formed by the action of ethyl iodide on the silver salt, is a colourless liquid of faint aromatic odour, boiling at 199–201°.

3. *Isopyrotartaric Acid from Isobutyric Acid (β -Isopyrotartaric Acid).*—This acid crystallises in transparent four-sided prisms, sparingly soluble in alcohol and moderately soluble in water. At 120° it sublimes in white needles, and at 170° begins to melt and decompose into carbon dioxide and isobutyric acid.

The *sodium salt* crystallises in small needles easily soluble in water.

The *barium salt* is less easily soluble and crystallises in stellate groups of thin needles.

The *calcium salt*, like that of the α -acid, is moderately soluble in cold water and is deposited from the solution on warming. It crystallises in nodules.

The *magnesium salt* is crystalline and easily soluble in water.

The *zinc salt*, $C_4H_4O_4 \cdot Zn \cdot 3H_2O$, obtained by saturating the acid with zinc carbonate, dissolves in 106 parts of water. It resembles the zinc salt of the α -acid and decomposes in the same manner.

The *lead salt*, produced on adding lead acetate to a hot solution of the sodium salt forms white scales, insoluble in hot and cold water.

The *silver salt* crystallises in small needles insoluble in water and not affected by boiling.

4. *Normal Pyrotartaric Acid.*—This acid, obtained by acting on propylene bromide with potassium cyanide at 100°, and then proceeding as in the preparation of α -isopyrotartaric acid, crystallises from water in large transparent four-sided prisms which melt at 97.5°. It distils for the most part at 215°, the distillate forming a white crystalline mass melting at 82°.

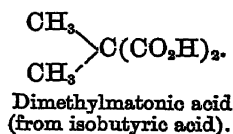
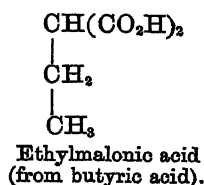
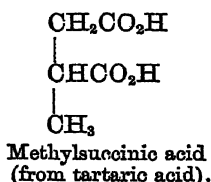
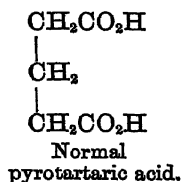
The *calcium salt*, which is more freely soluble in cold than in hot water, crystallises in stellate groups of thin needles.

The *magnesium salt* is crystalline, and easily soluble in water.

The *zinc salt* dissolves very sparingly in cold, and still less freely in hot water.

This acid appears to be identical with Dittmar's pyrotartaric acid, obtained by the reduction of glutanic acid, the salts of the two acids behaving in the same manner.

The foregoing results set at rest the question of the isomerism of the dicarbon acids of the formula $C_5H_8O_4$. The four theoretically possible isomerides are now all known. Their structural formulæ are as follows:—



J. R.

On Normal Oxypyrotartaric Acid (Glutanic Acid) and its Isomerides. By W. MARKOWNIKOFF (*Liebig's Annalen*, clxxxii, 347—358).—The author prepares glutanic acid by the action of nitrous acid on glutamic acid, the best result being obtained by adding potassium nitrite in the required quantity to a dilute solution of glutamic acid mixed with hydrochloric acid. Glutanic acid, being very soluble, is obtained in crystals with difficulty. The crystals melt at 72—73°, and solidify, on cooling, in a clear amorphous mass. The acid appears to form with bases two classes of neutral salts differing in solubility.

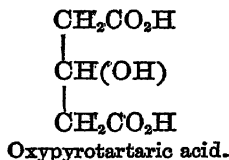
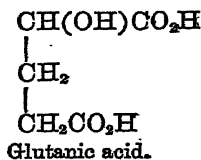
The *zinc salt*, obtained by saturating the acid with zinc carbonate, crystallises from a syrupy solution, on standing, in transparent four-sided tables, which when dissolved in hot water are transformed into a pulverulent sparingly soluble salt. It crystallises from a hot saturated solution in nodules agreeing in composition with the formula $C_5H_8O_4Zn + 3H_2O$.

The *magnesium salt*, $C_5H_8O_4Mg + 4H_2O$, obtained in the same manner as the zinc salt, is sparingly soluble in cold water, and crystallises from hot solutions in transparent microscopic rhombic tables.

Glutanic acid, when heated to 190°, is converted into an anhydride, which dissolves in water, reproducing the acid.

Glutanic acid is converted by reduction into normal pyrotartaric acid. It is isomeric with Maxwell Simpson's oxypyrotartaric acid

from dichlorhydrin. The structural formulæ of these bodies are as follows:—



The author discusses also the probable formulæ of itamalic and citramalic acids, two other isomerides of glutanic acid, but as yet the constitution of these bodies cannot be determined with certainty.

J. R.

Conversion of Citraconic Anhydride into Xeronic Anhydride. By R. FITTIG (*Deut. Chem. Ges. Ber.*, ix, 1189).—The author formerly described as xeronic anhydride a body formed in the distillation of citric acid. Further investigation of this body has shown that it is a product of the decomposition of citraconic anhydride (see this Journal, 1876, i, 898).

When pure citraconic anhydride is gently heated in a retort, it begins to evolve carbon dioxide at 160°, and on continuing the heating till the temperature gradually rises to 190°, the contents of the retort become converted into a brown very viscid mass, which when distilled yields first a small quantity of citraconic anhydride, and afterwards, at 220—270°, a brown oil insoluble in water, a carbonaceous residue being left in the retort. The brown oil, when distilled with water, yields a distillate of xeronic anhydride, the amount of which is comparatively small.

J. R.

Product of the Oxidation of Glycogen with Bromine, Silver Oxide, and Water. By R. H. CHITTENDEN (*Liebig's Annalen.*, cxxxii, 206—213).—The author has obtained, by the action of bromine on an aqueous solution of glycogen at 100°, and subsequent treatment of the product with silver oxide, an acid which he proposes to call *glycogenic acid*. It forms when pure an intensely sour syrupy liquid, the aqueous solution of which dissolves carbonates, forming salts having the general formula $\text{C}_6\text{H}_{11}\text{M}'\text{O}_7$ and mostly crystalline. The calcium, barium, cadmium, cobalt, manganese, and lead salts have been analysed. In all but the last ($\text{C}_6\text{H}_5\text{Pb}_2\text{O}_7$) the acid appears to be monobasic. The formation of the acid by the oxidation of glycogen may be represented as follows:—



Glycosamine Hydrochloride. By G. LEDDERHOSE (*Deut. Chem. Ges. Ber.*, ix, 1200).—When purified chitin is heated for half an hour with pure strong hydrochloric acid, it dissolves completely, forming a blackish-brown solution, which when evaporated leaves a large quantity of brilliant crystals mixed with a black amorphous mass. If chitin be similarly treated with addition of metallic tin

the solution formed has only a slight yellowish-brown colour, and the formation of the amorphous substance is entirely avoided. The crystals amount to about 40 per cent. of the chitin employed. Their composition agrees with that of a carbohydrate in which HO is replaced by NH_2 , combined with hydrogen chloride.



The crystals, which have a decidedly sweet taste, dissolve freely in water, sparingly in alcohol, forming acid solutions. They give with soda-ley and copper sulphate a dark-blue solution, which deposits cuprous oxide on warming. The substance is being further examined.

J. R.

New Derivatives of Mucic Acid. By RUDOLPH FITTIG (*Deut. Chem. Ges. Ber.*, ix, 1198).—Mucic acid is decomposed by fuming hydrobromic acid when heated therewith for some days in the water-bath. The chief product of the reaction is an acid crystallising from water in long silky needles and from alcohol in laminæ, and agreeing in composition with the formula $\text{C}_6\text{H}_4\text{O}_5$. Its formation may be represented by the equation—



in accordance with which the author calls it *dehydromucic acid*.

The *barium salt*, $\text{C}_6\text{H}_2\text{O}_5\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$, crystallises in tufts of needles sparingly soluble in cold water. The *calcium salt*, $\text{C}_6\text{H}_2\text{O}_5\text{Ca} + 3\text{H}_2\text{O}$, forms colourless laminæ or small transparent needles. The *silver salt*, $\text{C}_6\text{H}_2\text{O}_5\text{Ag}_2$, is a white precipitate insoluble in water.

The *ethyl ether*, $\text{C}_6\text{H}_2\text{O}_5(\text{C}_2\text{H}_5)_2$, crystallises from alcohol in colourless rhombic prisms, dissolving easily in alcohol and ether, and melting at $46-47^\circ$. It is not affected by heating with acetic anhydride.

The acid is converted by the action of sodium-amalgam into a new acid, which is crystallisable and easily soluble, and melts at about 140° .

Dehydromucic acid, when carefully heated, distils for the most part undecomposed, without melting; but when distilled in a bent tube it breaks up almost entirely into carbon dioxide and pyromucic acid.



J. R.

On the Preparation of Levulinic Acid and on Caragheen-sugar. By F. BENTE (*Deut. Chem. Ges. Ber.*, ix, 1157—1158).—This acid is formed not only by boiling cane-sugar or inulin with dilute sulphuric acid, but is also obtained from filter-paper, wood, Caragheen-moss, and left-handed gum-arabic. The latter yields, at the same time, a small quantity of Scheibler's arabinose, and caragheen, an *inactive* sugar, which reduces copper and silver salts, and is oxidised by nitric acid to oxalic acid. The isomeric silver levulinate, which the author formerly described, does not exist, being only the impure ordinary salt (see this Journal, 1875, 1005).

C. S.

and a New Case of the Complete Transformation of that Acid. By J. DE GIRARD (*Compt. rend.*, lxxxiii, 344).—It is known that anhydrous hydrocyanic acid sometimes suffers decomposition in a very short time, whereas at other times it may be kept for months without change. This difference arises from the calcium chloride used in drying the acid. If the calcium chloride is neutral, the acid obtained will be pure; but if the chloride is alkaline, as it is when ignited in the open air, the acid rapidly decomposes spontaneously. The explanation is that on the contact of the acid with the lime contained in the ignited calcium chloride, calcium cyanide is formed; this, with the water contained in the hydrocyanic acid, gives rise to the formation of calcium formate and ammonia, and it is known that a trace of ammonia is sufficient to determine the decomposition of the anhydrous hydrocyanic acid.

If some pure anhydrous acid be heated in a sealed tube for four or five hours, the liquid solidifies to a compact black mass. On opening the tube, there is no evolution of gas, and the black substance has the total weight of the acid employed, and the same centesimal composition. On heating it in a tube open at one end, ammonium cyanide is at first formed, then cyanogen, and a carbonaceous residue is left; but it may be heated to 50° without alteration.

On treating the black substance with ether, a crystallisable body is obtained, upon which further experiments are in progress.

C. H. P.

Decomposition of Potassium Cyanide, Zinc Cyanide, and Potassium Formate, in Carbonic Acid, Air, and Pure Hydrogen. By L. NAUDIN and F. DE MONTHOLON (*Compt. rend.*, lxxxiii, 345).—Carbonic acid completely decomposes potassium cyanide in aqueous solution. With a solution containing about 3 per cent. of the salt, and a regular current of carbonic acid, the quantities of cyanide decomposed were found to be equal for equal intervals of time.

Decomposition of Potassium Cyanide in Pure Hydrogen, and in Air Deprived of Carbonic Acid.—A solution containing 2.17 per cent. of the salt as HCy, was employed, through which hydrogen was passed. After 36 hours, the loss of HCy amounted to 5.8 per cent. The decomposition still proceeded, but so slowly, that the loss of hydrocyanic acid was undeterminable. The limit of 5.8 per cent. was attained more rapidly in proportion as the current of hydrogen was itself more rapid. At a temperature of 15°, no formic acid was produced; but at 60–80°, a notable quantity of potassium formate was obtained, but as this body decomposes at that temperature, the progress of the reaction could not be followed.

Air gave identical results.

The decomposition of potassium cyanide in an inert gas is limited only by the alkalinity of the remainder, due to the potash liberated; with carbonic acid, there is no limit, because the alkali is neutralised as rapidly as it is produced.

Decomposition of Zinc Cyanide and Potassium Formate in Carbonic Acid, Pure Hydrogen, and Pure Air.—Zinc cyanide, suspended in dis-

tilled water, suffered slow decomposition by a rapid current of carbonic anhydride. With air deprived of carbonic anhydride, a very slight but noticeable decomposition occurred. No trace of decomposition was noticed in the cases of uranium and nickel cyanides, even by the prolonged action of carbonic anhydride; but that gas decomposes potassium formate, as also do pure hydrogen and air, though in a less degree.

C. H. P.

The Structure of Cyanic and Cyanuric Acids. By A. CLAUS (*Deut. Chem. Ges. Ber.*, ix, 1165—1167).—The author maintains, against Nencki and Fleischer, that these acids are hydroxyl-compounds.

C. S.

Chloral Cyanide-cyanate and its Derivatives. By C. O. CRECH (*Deut. Chem. Ges. Ber.*, ix, 1253—1255).—The formation of this substance has been described by the author in a previous paper (see this Journal, 1876, i, 376; also ii, 66). It dissolves sparingly in cold, and easily in hot water, being completely decomposed thereby, with formation of hydrocyanic and formic acids. On heating it with water in sealed tubes, hydrocyanic acid is eliminated, and the liquid yields ammonium chloride on evaporation. The substance dissolves in dilute acids and crystallises therefrom unaltered, but when heated with dilute hydrochloric acid, it yields ammonium chloride. When distilled with water, it is resolved into hydrocyanic and hydrochloric acids, carbon dioxide, and formic acid. Heated *per se* in a closed tube, it sublimes partially in long needles at 100°, and carbonises at 120°.

In the reaction of chloral, potassium cyanide, and potassium cyanate, there is formed, together with the foregoing compound, a body having the formula $C_4H_3Cl_2N_2O_2$, and therefore differing from it by the elements of 1 mol. of hydrogen chloride. This substance, previously described by Wallach (see this Journal, 1876, i, 376), forms small yellow needles, soluble in alcohol, ether, and water. The author has found that it is formed whenever chloral cyanide-cyanate remains suspended in a solution of potassium cyanide. It dissolves in sodalyle, and is precipitated unaltered by acids. When heated with alkalis, it evolves ammonia. Heated with dilute hydrochloric acid, it is converted into fine laminae of a substance which dissolves in water, alcohol, and ether, and crystallises therefrom in yellow needles, agreeing in composition with the formula $C_4H_3Cl_2NO_4$. The formation of this substance may be represented thus:

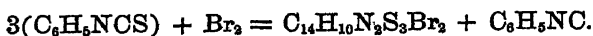


The needles melt at 154°, sublime partially in beautiful rhombic tables, dissolve in ammonia and dilute acids, and crystallise from the latter unchanged.

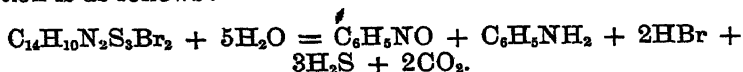
J. R.

Action of Bromine on Phenyl Sulphocyanate. By B. PROSKAUER and EUG. SELL (*Deut. Chem. Ges. Ber.*, iv, 1262—1266).—When a solution of bromine in chloroform is added to phenyl sulphocyanate diluted with chloroform, an orange-red crystalline sub-

stance is formed, the composition of which agrees with the formula $C_{14}H_{10}N_2S_3Br_2$. At the same time, some phenyl isocyanide is formed. The reaction is probably represented by the equation—



The former product dissolves quietly in water in the cold, but at 100° , a violent reaction occurs, in which large quantities of carbon dioxide and hydrogen sulphide are evolved, and aniline hydrobromide and the hydrobromide of another base, C_6H_5NO , are formed. The reaction is as follows:—

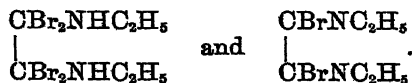


The base, $C_6H_5NO_2$, crystallises in white needles, which dissolve sparingly in water and easily in alcohol. It forms, with platinum tetrachloride, a crystallisable double salt. Its melting point is 156° .

With alcohol, the orange-red body behaves quite differently. At the boiling heat, a violent reaction takes place, in which ethyl bromide and hydrobromic acid are formed, and part of the alcohol is oxidised. The liquid, on cooling, deposits beautiful sulphur-yellow needles, agreeing, when purified, with the formula $C_{14}H_{10}N_2S_3$, melting at 152° , and dissolving freely in hot alcohol, but not in water. The same product is formed by the action of glacial acetic acid on the orange-red body. Its constitution is not yet determined. The authors are continuing their investigation. J. R.

Action of Alcoholic Potash on the Mustard Oils (Sulphocarbimides). By R. SCHIFF (*Deut. Chem. Ges. Ber.* ix, 1316).—By this reaction the same sulphocarbamic ethers are formed that Hofmann obtained by heating the sulphocarbimides with absolute alcohol to 110° . Thus a mixture of phenylic sulphocarbimide and alcoholic potash becomes hot, and then the compound $CS \begin{cases} OC_2H_5 \\ NH.C_6H_5 \end{cases}$ separates out. Allylic sulphocarbimide is even more readily acted upon by alcoholic potash. C. S.

Action of Phosphorus Pentabromide on Amides. By O. WALLACH (*Deut. Chem. Ges. Ber.* ix, 1213).—Diethyloxamide reacts with phosphorus pentabromide at a gentle heat, to form two crystalline bodies, which may be represented by the formulæ.



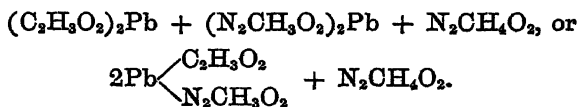
These substances are decomposed by water, and react with ammonia to form diethyloxamide. When heated, they give off hydrogen bromide and yield a brown mass, from which potash liberates the base *brom-oxaethylin*. This last is a solid body, which distils with difficulty.

J. R.

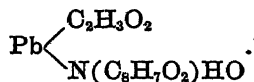
On Salts of Hydroxylurea and Double Salts of other Hydroxamates. By N. D. C. HODGES (*Liebig's Annalen*, clxxxii, 214—220).—Dresler and Stein, who first investigated hydroxylurea, were unable to obtain compounds of that substance with acids. Derivatives of hydroxylamine corresponding with amides having since been shown to possess acid properties, it is improbable that hydroxylurea is capable of combining with acids: it might rather be expected to contain hydrogen replaceable by metals, and the results of experiments made by the author seem to show that such is the case.

Sodium and Potassium Salts of Hydroxylurea.—When a solution of hydroxylurea in absolute alcohol is mixed with a solution of potassium hydrate or of metallic sodium in absolute alcohol, a colourless precipitate is thrown down, which rapidly becomes pasty, and absorbs moisture greedily from the air. On one occasion the potassium compound was obtained as a crystalline powder, which, after careful drying in a current of air, was found to contain 17·94 per cent. of potassium. By analogy with other hydroxamates, the formula of the potassium salt should be $N_2CH_3KO_2 + N_2CH_4O_2$, which requires 20·56 per cent. of potassium.

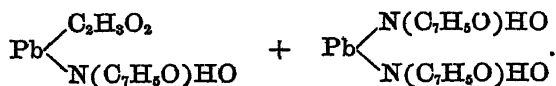
Lead Salt of Hydroxylurea and Acetic Acid.—When to an aqueous solution of the sodium salt obtained as above, an excess of neutral lead acetate is added, the solution deposits on standing small colourless crystals agreeing in composition with the formula,



Lead Acetate and Anishydroxamate.—Acid potassium anishydroxamate added to excess of a strong solution of neutral lead acetate throws down a dense white precipitate, the composition of which, after drying, agrees with the formula.



Lead Acetate and Benzhydroxamate.—Obtained in the same manner as the preceding compound. A dense white precipitate, agreeing in composition with the formula.

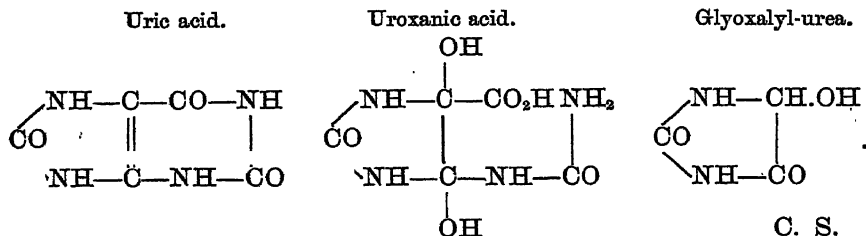


J. R.

Decomposition of Uroxanic Acid. By L. MEDICUS (*Deut. Chem. Ges. Ber.* ix, 1162—1164).—On boiling this acid with water, no allantoinic acid is formed, as Mulder has stated, the products consisting of urea, carbon-dioxide and glyoxalyl-urea.



This decomposition confirms the views which the author held as to the constitution of uric and uroxic acids.



Two new Thiocarbamides (Sulphureas). By PH. DE CLERMONT and E. WEHRLIN (*Compt. rend.*, lxxxiii, 347).—These were produced by a reaction similar to that signalled by one of the authors for the preparation of phenylthiocarbamide, which consisted in heating aniline hydrochloride with ammonium sulphocyanide.

Cresylthiocarbamide, $\text{CS.NH}_2.\text{NH.C}_7\text{H}_7$.—Hydrochloride of paratoluidine is heated with ammonium thiocyanide, on the water-bath, in presence of water. After a brief space an insoluble substance separates. This is washed on a filter until the washings afford no reaction with a ferric solution, and then dissolved in boiling alcohol, which, on cooling, deposits the cresylthiocarbamide in crystals. These crystals are colourless plates, which melt at 188° , have a persistent bitter taste, and are scarcely soluble in water or ether.

Naphtylthiocarbamide.—Prepared in the same manner as the last, substituting naphtylamine for the toluidine. It crystallises in small prisms with rhombic base, which melt at 198° , are slightly soluble in water and ether, and very soluble in boiling alcohol. They have a bitter flavour, and become brown on exposure to the air. Heated with lead oxide in boiling alcohol, the substance is completely desulphurised, and a crystalline body is produced, which is under examination.

If to a solution of naphtylthiocarbamide in sulphuric acid a little nitric acid is added, nitrous vapours are evolved, and a flocculent yellow substance produced which is slightly soluble in water, but very soluble in alcohol. It has an intense tinctorial power, and dyes silk a beautiful yellow. The formula of naphtylthiocarbamide is $\text{CS.NH}_2.\text{NH.C}_{10}\text{H}_7$.

C. H. P.

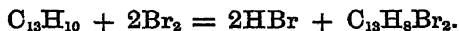
On Fluorene and Pyrogenic Hydrocarbons. By PHILIPPE BARBIER (*Ann. Chim. Phys.* [5], vii, 472—546).—The author commences by briefly referring to the results of various chemists who have isolated or otherwise examined the hydrocarbons fluorene, anthracene, phenanthrene, and tolane: the last-named three isomerides may all be formed synthetically from toluene, and may legitimately be considered as derived by dehydrogenation from the hydrocarbons $\text{C}_{14}\text{H}_{14}$.

Fluorene, isolated some years ago by Berthelot from the heavy oils of coal tar boiling between 280 and 340° , has been prepared in some quantity by the author and carefully examined. It is best prepared from the heavy oils from which anthracene and naphthalene have

separated, by first submitting them to fractional distillation, and collecting the portion passing at 290—340° (the distillate at 270—290 contains much acenaphthene); by a further series of fractionations a portion passing at 300—320° is isolated. To obtain a good result, enough oil should have been originally employed to allow of 15 or 20 liters of this distillate being collected. By the action of cold, this fraction becomes nearly solid; the mass is pump-filtered, and the solid residue pressed in blotting paper, and then again distilled, collecting what passes at 290—310°. Above this temperature little but phenanthrene passes over, this hydrocarbon being thus obtained in an almost pure state; it constitutes about one-half of the pressed crystals. On again distilling and collecting at 295—305°, a yellowish-white mass is obtained containing a little oxidized substance and some acenaphthene; these are eliminated by successively crystallising from a mixture of benzene and alcohol, alcohol alone, and glacial acetic acid. The last-named solvent removes the oxidized substance, but the same result can also be obtained by exposing to sunlight a solution of the crude fluorene in benzene.

Absolutely pure fluorene may be prepared from the nearly pure substance thus obtained by dissolving it in ether, and adding the requisite quantity of picric acid. On slow evaporation fine red needles of the picric acid compound of the hydrocarbon separate, melting at 80—82°; by treating these with ammonia the hydrocarbon is set free; and by repeating the combination with picric acid and regeneration several times, a perfectly pure body, melting at 113°, is obtained.

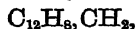
Fluorene thus obtained boils at about 305°; it sublimes with difficulty in very small white plates, agglomerated so as to look like small white granules. It is very soluble in ether, benzene, carbon disulphide, and hot alcohol; in cold alcohol it is only sparingly soluble. The crystallised product has a beautiful violet fluorescence. On analysis it gives numbers leading to the formula $C_{13}H_{10}$ *—a result confirmed by the quantity of picric acid contained in the picrate, and by the analysis of *dibromofluorene*—a well-crystallised characteristic derivative obtained by adding the calculated quantity of bromine dissolved in carbon disulphide to a solution of fluorene in the same menstruum. By distillation a residue is left which is freed from a red bye-product by washing with ether; the insoluble substance is then crystallised twice from carbon disulphide by spontaneous evaporation. The crystals belong to the clinorhombic or monoclinic system, and melt at 166—167°; they distil unchanged at a high temperature, and are not attacked by boiling alcoholic potash. They are nearly insoluble in ether and in alcohol, but dissolve readily in carbon disulphide and in chloroform. This bromo-derivative is formed by the reaction.



When heated with red-hot lime, it forms *diphenyl* melting at 60°, and produces lemon-yellow rhomboidal plates, with Fritzsche's re-

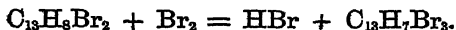
* The author throughout his paper employs the combining numbers $O = 6$ and $O = 8$, and adheres to the system of formulæ used by Berthelot, of whom he is a disciple. He accordingly represents fluorene by the formula $C_{26}H_{20}$ and fluorenic alcohol by $C_{26}H_{22}(H_2O_2)$.

agent (dinitranthraquinone): hence the author regards fluorene as a *diphenyl-methylene*,

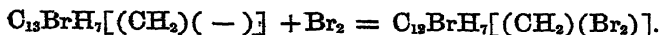


i.e., as "diphenyl in which H_2 is replaced by an equal volume of methylene."

If an excess of bromine be employed in the production of dibromofluorene, or if that body be heated with bromine, hydrobromic acid is evolved and *tribromofluorene* formed thus:—

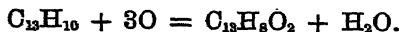


It is somewhat difficult to obtain this body free from the dibromo derivative; when pure it melts at $161-162^\circ$. A *tetrabromofluorene* and a *dibromide of monobromofluorene* $C_{13}H_5Br(Br_2)$ have also been obtained, the latter by avoiding all heating when fluorene and bromine are brought together, this being accomplished by passing air charged with bromine vapour slowly into a solution of fluorene in carbon disulphide. This body forms silky yellow needles, soluble in benzene, but decomposed on frequent crystallisation, forming hydrobromic acid and dibromofluorene; this result is instantly brought about by contact with alcoholic potash. The production of this addition-product is, according to the author, quite in accordance with the constitution assigned to fluorene; bromodiphenyl-methylene should be capable of taking up Br_2 ; thus:



When nitric acid acts on fluorene, *mono-nitrofluorene* and *dinitrofluorene* are produced; the former is a red powder not easily obtained in the crystalline state; the latter a reddish-yellow mass of needles difficultly soluble in ordinary solvents, but crystallisable with difficulty from a mixture of nitrobenzene and light oils: when treated with reducing agents, it forms an alkaloïdal substance (*Diamine of fluorene?*). Sulphuric acid forms with fluorene a sulpho-acid the salts of which are either non-crystalline, or crystallisable only with difficulty.

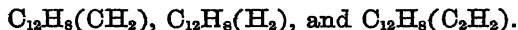
Chromic acid dissolved in acetic acid, or a mixture of potassium dichromate and sulphuric acid, attacks fluorene only with difficulty; after long action there are formed, besides formic, oxalic, and phthalic acids, two new bodies—*fluorene-quinone* and *diphenylene carbonyl*. These are nearly insoluble in water, and are separated by means of a warm mixture of alcohol and benzene. On cooling, grains of the former separate, whilst the latter remains in solution; by recrystallisation of these grains from benzene, fluorenoquinone is obtained pure; it is formed by the reaction,



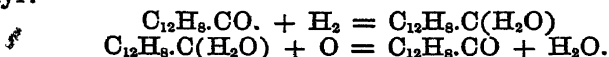
Fluorenequinone melts at $181-182^\circ$: sulphurous acid solution at 100° gives a crystalline product, probably fluorene-hydroquinone; when it is heated to 180° with iodine and phosphorus, fluorene is regenerated.

Diphenylene-carbonyl, $C_{13}H_8CO$, melts at $81-82^\circ$. When treated with melting potash it forms *diphenylformic acid*, $C_{13}H_8CH_2O_2$, the calcium salt of which gives rise to diphenyl by dry distillation. Appar-

ently, therefore, this oxidation-product of fluorene is identical with the "diphenylenacetone" of Fittig and Ostermayer, prepared from diphenyl-oxalic acid (an oxidation-product of phenanthrene). Hence the relationships between fluorene, diphenyl, and phenanthrene are expressed by the formulæ—



By acting on diphenylene-carbonyl (prepared from phenanthrene, which is easier) with nascent hydrogen, *fluorenic alcohol* is formed; after crystallisation from benzene, this alcohol forms hexagonal plates melting at 153° ; it is soluble in alcohol and ether, more so in benzene; oxidising agents convert it into diphenylene-carbonyl, *i.e.*, it behaves like a secondary alcohol. The following equations represent the formation of the alcohol, and its subsequent reconversion into diphenylene carbonyl:—



By the action of acetic anhydride at 100° , fluorenic alcohol forms *fluorenic acetate*, a crystallisable body melting at 75° , and capable of saponification by baryta-water at 120° , with formation of barium acetate and reproduction of the alcohol. When heated to a temperature a little below its melting point, either alone or, preferably, with acetic anhydride, fluorenic alcohol loses water and forms *fluorenic ether*—



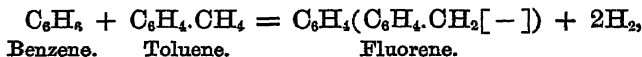
The ether thus formed is a nearly colourless resinous body melting at about 290° , very soluble in benzene, but only sparingly soluble in alcohol and ether. These properties of fluorenic alcohol result, according to the author, from the double functions it possesses, arising from its being not only a hydrogenised carbonyl (*i.e.*, an incomplete ketone), but also a derivative of a non-saturated hydrocarbon; wherefore it exerts the functions of a pseudo-alcohol of incomplete character, and is capable of parting with water, whilst it can also polymerise, the two actions taking place simultaneously.

Together with fluorenic alcohol there is formed, on hydrogenising diphenylene carbonyl with sodium amalgam, a small quantity of a body somewhat more soluble in benzene, and crystallising in fine needles. Not improbably this body is the relatively complete body of the series formed by the fixation of $2H_2$ on diphenylene carbonyl, and bearing to fluorenic alcohol the same relation as pseudo-propylic alcohol to allylic alcohol.

When fluorene is heated to about 275° with ten times its weight of a solution of hydriodic acid saturated at 0° , carbon is set free, together with various hydrocarbons of less complex character than fluorene; benzene and toluene are thus produced, together with a hydrocarbon boiling near 220° , and entirely soluble in fuming nitric acid. If a larger quantity of hydriodic acid be used (40 parts), hexane and heptane and a tridecane, $C_{13}H_{26}$, are formed, together with a minute quantity of a hydrocarbon volatile at about 360° . The tridecane thus produced is not attacked either by nitric acid, cold bromine, or fuming

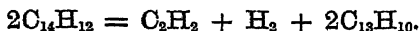
sulphuric acid; it can also be formed by heating to 200° fluorene and red phosphorus with hydriodic acid of sp. gr. 1.5.

In the hope of synthesizing fluorene from a mixture of benzene and toluene at a red heat, in virtue of the reaction—



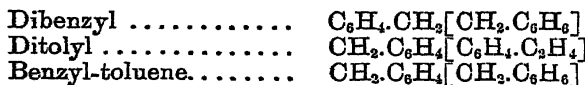
the author passed the vapour of a mixture of these hydrocarbons through a red-hot tube, but with no decisive result; a minute quantity of a body boiling near 301°, and possessing fluorescent properties, was formed, but the greater portion became converted into diphenyl and anthracene. With the same object in view the isomeric hydrocarbons, $\text{C}_{12}\text{H}_{12}$, diphenyl-methane and phenyl-toluene (from liquid bromo-toluene and phenyl bromide by the action of sodium) were heated in sealed tubes wrapped in wire gauze to a dull red heat, the air in the tubes having been withdrawn by a pump before sealing the tubes; no fluorene, however, was produced in either case. The phenyl-toluene used was found to boil at 255–260° after purification by fractional distillation. Like its isomeride, diphenyl-methane, it yielded benzene and toluene in the sealed tube; a viscid hydrocarbon boiling at about 300° was also formed with phenyl-toluene, whilst diphenyl-methane gave rise to much anthracene.

The author considers that fluorene is formed in coal-tar by an alteration of phenanthrene, which he supposes first to assimilate hydrogen, forming phenanthrene hydride, $\text{C}_{14}\text{H}_{12}$, which then splits up into acetylene, hydrogen, and fluorene, thus:—



No experimental evidence in support of this view is, however, adduced.

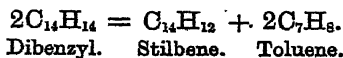
Action of Heat on Hydrocarbons derived from a Double Molecule of Toluene by elimination of Hydrogen.—The isomerides $\text{C}_{14}\text{H}_{14}$, dibenzyl, ditolyl and benzyl-toluene, are represented thus—



all these being capable of being regarded as being formed from toluene by elimination of hydrogen, thus:—



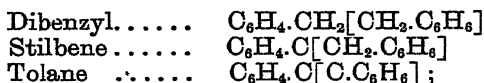
In order to trace out the relationships between these substances and the three isomerides $\text{C}_{14}\text{H}_{10}$, anthracene, phenanthrene, and toluene, the former hydrocarbons were heated to 500–600° in sealed empty tubes as above described. In this way dibenzyl gave rise to *toluene*, and *stilbene*, $\text{C}_{14}\text{H}_{12}$, thus:—



By the same means stilbene gave rise to *toluene* and *phenanthrene*—



no toluene being found, although the production of that body would seem *à priori* probable, since the relationships of dibenzyl, stilbene, and toluene are represented by the formulæ—



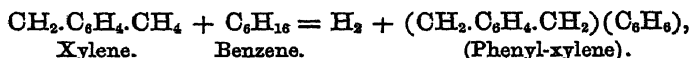
phenanthrene being $\text{C}.\text{CH}_2[\text{C}_6\text{H}_4.\text{CH}_2]$, since the author finds that on heating toluene with hydriodic acid and red phosphorus to 180° stilbene is formed. The phenanthrene, therefore, is produced on heating stilbene by a sort of “intramolecular movement” analogous to that whereby ethyl-benzene becomes transformed into dimethyl-benzene at a high temperature (Berthelot). Toluene itself when heated in a sealed tube to 500° is almost wholly carbonised, a little benzene and traces of what seems to be diphenyl being formed, but no phenanthrene or other hydrocarbon.

Ditolyl prepared from solid bromotoluene and sodium gave rise, when heated to 500 – 600° in a sealed tube, to no decomposition at all during a short exposure; but after the lapse of a longer time it was wholly destroyed, hydrogen being evolved and carbonisation taking place, but neither anthracene nor phenanthrene being formed. Simultaneously with the crystallisable ditolyl prepared from solid bromotoluene, the author found that a liquid isomeride, called by him β -ditolyl, is formed in small quantity. This is different from the ditolyl previously known, prepared from liquid bromotoluene, inasmuch as when heated in a sealed tube, it is wholly destroyed, like the solid ditolyl, whilst ditolyl from liquid bromotoluene (α -ditolyl of the author) forms under the same conditions *toluene*, *anthracene*, and *phenanthrene*, the second hydrocarbon constituting the greater portion of the product. The mixture of anthracene and phenanthrene thus produced was found to give with Fritzsche’s reagent brown rhomboidal plates exactly resembling those assigned to the “phorene” of that chemist, whilst the pure hydrocarbons separated by repeated crystallisation from this supposed phorene gave entirely different products, anthracene forming rose-violet plates, and phenanthrene clear yellow ones: hence the author concludes that “phorene” is not, as Fritzsche supposed, a single hydrocarbon isomeric with anthracene, but is simply a mixture of phenanthrene and anthracene, the more so as a mixture of perfectly pure anthracene with pure phenanthrene formed brown rhomboidal plates with Fritzsche’s reagent.

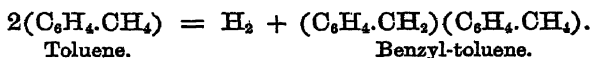
Benzyl-toluene as prepared by acting on benzyl chloride with zinc in presence of toluene, is a mixture of two isomerides both represented by the formula $\text{CH}_2.\text{C}_6\text{H}_4[\text{CH}_2.\text{C}_6\text{H}_5]$ (just as the three ditolyls above mentioned are all represented by $\text{CH}_2.\text{C}_6\text{H}_4[\text{CH}_2.\text{CH}_3]$): the author did not attempt to separate these two, but heated the mixture boiling at 277° in a sealed tube. The products were *toluene* and *anthracene*, formed from one modification of the benzyl-toluene, while from the other modification which remained unaltered under the conditions of the expe-

periment, a minute amount of phenanthrene was apparently also formed, as the plates thrown down by Fritzsche's reagent were not of a pure rose-violet colour, but consisted of a mixture of rose-violet plates with brown ones.

To complete the history of the pyrogenic derivatives of the hydrocarbons $C_{14}H_{14}$, the author synthesized a new isomeride, *phenyl xylene*, by Zincke's method, viz., acting on tolyl chloride (prepared by the action of chlorine on xylene vapour, and boiling at $192-196^\circ$) with zinc in presence of benzene. After several fractionations a product was obtained boiling between 270° and 280° , and giving numbers agreeing with the formula $C_{14}H_{14}$. To this body the author assigns the formula $(CH_2.C_6H_4.CH_2)(C_6H_6)$, regarding it as being formed by the reaction—



whilst benzyl toluene is formed by the reaction—

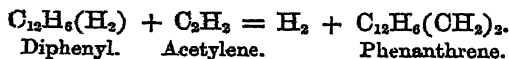


On heating this phenyl-xylene to $500-600^\circ$ in a sealed tube, there were obtained *benzene*, *xylene*, and *anthracene*, apparently containing a little *phenanthrene*, as brown plates were obtained with Fritzsche's reagent.

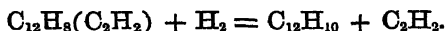
It hence appears that in pyrogenic actions anthracene may be formed, not only by the dehydrogenation of a double molecule of toluene (or of a hydrocarbon such as benzyl-toluene of the same degree of carbon condensation), but also by the similar reaction between benzene and xylene.

A fraction of hydrocarbons boiling at $245-250^\circ$ was isolated from coal-tar and deprived of solid hydrocarbons by methodical precipitation with picric acid. The liquid thus obtained consisted of a mixture of saturated hydrocarbons of high boiling point (paraffins?) and other hydrocarbons of character analogous to the $C_{14}H_{14}$ hydrocarbons. On heating this mixture to $500-600^\circ$ in sealed tubes, there were obtained *acenaphthene* and a little *benzene* and *naphthalene*, whence it is manifest that the coal-tar hydrocarbons of more saturated character split up under the influence of heat into less condensed carbon groups, just as do the hydrocarbons above examined.

Phenanthrene. Regarding this hydrocarbon as diphenyl in which H_2 is replaced by acetylene, the author tried to synthesize it by passing through a red-hot tube a mixture of diphenyl vapour and ethylene. The products of the reaction were *benzene*, *styrolene*, and *naphthalene*, arising from the condensation of the acetylene formed by the action of the heat on the ethylene, the first also arising from the decomposition of diphenyl. In addition *unthracene* and *phenanthrene* were formed, the latter constituting the main portion of the whole product. Hence the reaction was—



In the hope of preparing the phenanthrene hydride described by Græbe, the author heated together to 210—240° phenanthrene and hydriodic acid, but without any result. At 260° a liquid was formed, consisting of unaltered phenanthrene and a paraffin, $C_{14}H_{30}$, not attacked by nitric acid, cold bromine, or sulphuric acid. Hence the author concludes that Græbe's product was not a single hydrocarbon, $C_{14}H_{12}$, but only a mixture of this tetradecane and unchanged phenanthrene; although he thinks phenanthrene hydride is formed in small quantity when sodium amalgam acts on an alcoholic solution of phenanthrene. The mixture of phenanthrene and the product of its hydrogenation by hydriodic acid was heated in a sealed tube to 500°; *diphenyl*, *benzene*, and a little phenanthrene were formed by the inverse reaction of that by which phenanthrene is synthesized, viz.:—



The acetylene thus produced, however, becomes forthwith polymerised into benzene.

Phenanthrene and anthracene are formed simultaneously, not only in the above-described cases, but also by the pyrogenous reaction of benzene and styrolene, and of ethylene and benzene. The anthracene formed by acting on benzyl chloride with water forms with Fritzsche's reagent the brown compound characteristic of a mixture of anthracene and phenanthrene, as does also the anthracene produced by reducing alizarin with zinc powder. The only reaction in which phenanthrene is formed without the production of anthracene is when stilbene is heated.

When benzyl sulphide is distilled, a body expressed by the formula $C_{14}H_{12}S$ is formed, to which the author applies the term *sulphostilbene*.

This substance forms light white plates melting at 168—169°, and readily subliming at a higher temperature. With Fritzsche's reagent it forms light yellow rhomboidal plates, and with picric acid it produces very unstable fine red needles. By oxidation it forms benzylic alcohol.

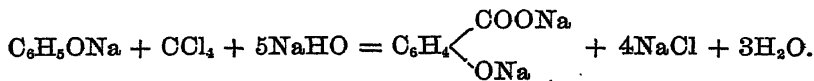
C. R. A. W.

Synthesis of Propyl-isopropyl-benzene. By E. PATERNO and P. SPICA (*Gazzetta chimica italiana*, vi, 99—100).—The authors find that a powerful reaction takes place when either benzyl chloride or cumenyl chloride is treated with zinc-ethyl, it being necessary to cool the zinc-ethyl with snow, and add the chloride drop by drop. With benzyl chloride a hydrocarbon was obtained, closely resembling in its properties the cumene from cuminic acid, but which, if Jacobsen's results are correct, must be isomeric with it. Cumenyl chloride gives a hydrocarbon, $C_9H_7.C_6H_4.CH_2.C_2H_5$, *propyl-isopropyl-benzene*. It is lighter than water, and boils at 205°—208°. The authors have not yet carefully examined these reactions, but have observed that condensation-products of high boiling point are formed at the same time.

C. E. G.

Action of Carbon Tetrachloride on Phenol in Alkaline Solution. By K. REIMER and FERD. TIEMANN (*Deut. Chem. Ges. Ber.*, ix, 1285—1287).—Carbon tetrachloride is but very slowly acted

on when heated with an aqueous solution of phenol in excess of alkali, but in alcoholic solution the reaction proceeds more rapidly. The products are salicylic and paraoxybenzoic acids, the formation of which is represented by the following equation :—



The authors employed in their experiments 28 parts of sodium hydrate or 36 parts of potassium hydrate, dissolved in a small quantity of boiling water, and mixed with so much alcohol that carbon tetrachloride produced no turbidity in the solution, together with 10 parts of crystallised phenol and 17 parts of carbon tetrachloride, the mixture being heated to 100° in sealed tubes for two or three days.

The relative amounts of salicylic and paraoxybenzoic acids produced were apparently not influenced by the nature of the alkali employed.

This reaction of carbon tetrachloride on phenol in alkaline solution corresponds exactly to that of chloroform, since it produces directly the same acids that are obtained by the oxidation of the aldehydes formed in the chloroform reaction.

J. R.

Preparation of Hydroquinone. By P. WESSELSKI and J. SCHULER (*Deut. Chem. Ges. Ber.*, ix, 1159—1161).—When diazophenol nitrate, which is obtained by the action of nitrous acid on a solution of phenol in ether, is dissolved in dilute sulphuric acid, and the solution mixed with alcohol and ether, the sulphate crystallises out, which by means of barium chloride, is readily converted into the hydrochloride. The diazophenol is identical with that which Schmitt obtained from the nitrophenol melting at 110°.

When the sulphate is boiled with water, a resinous body is formed, but on using dilute sulphuric acid (15—20 per cent.), hydroquinone is produced, a pure product yielding 46.2 per cent., instead of 50.

C. S.

Rotatory Powers of the Isomeric Camphols. By J. DE MONTGOLFIER (*Compt. rend.*, lxxxiii, 341).—The camphols of different origin, natural or artificial, differ from one another only by their rotatory power. This is explained by the fact that borneol consists of a mixture of an active and an inactive variety, the maximum rotation for the active one being + 37° for the ray D. It is easy to produce the variety having a high rotatory power, but the production of the other is by no means so certain, and as yet all efforts have failed to obtain a borneol wholly inactive. By the action of alcoholic potash on camphor, a borneol of very low rotatory power is obtained, such as 1° 41', 3°, and 5° 15'. By using alcohol more and more dilute, the rotatory power of the borneol is progressively increased, but other circumstances also affect the results, the study of which is not yet completed. By the act of combination, the rotatory power of borneol is augmented. Some pure borneol having a rotation of 14° 35',

was treated with stearic acid for ten hours at 200° . The portion not combined was removed, and found to have a rotatory power of 15° , whilst that obtained by decomposing the stearic borneol had a rotatory power of $22^{\circ} 18'$. This is evidently not a separation of the active from the inactive variety.

The augmentation of rotatory power is effected by the temperature at which the etherification takes place; the higher that temperature, the greater the rotatory power of the borneol subsequently eliminated.

Is this really a creation of rotatory power? The author thinks not, because the camphors produced by the action of nitric acid on borneols of any rotatory power always exhibit the same rotation, namely, about $44^{\circ} 40'$. These results cannot be explained on the hypothesis of an active and an inactive variety, without supposing a partial destruction of the inactive variety by the action of stearic acid, and its total destruction by conversion into camphor. But this is not borne out by experiment, because there are no products of destruction by the action of stearic acid, and the transformation of a nearly inactive borneol, such as of $1^{\circ} 30'$ rotation, ought to give only about one-twentieth of active camphor, whereas the quantity really obtained was far larger. The hypothesis of an ordinary inactive variety should therefore be abandoned. It is a new type; an active body in which the rotatory power is, so to speak, hidden, and is ready to be reproduced by the first action to which it is subjected, such as etherification, especially at high temperatures. Thus, the borneols, whether natural or artificial, would be mixtures of this particular inactive, and of the active varieties.

C. H. P.

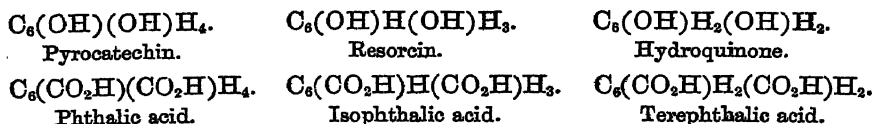
Crystalline Form, Specific Gravity, and Molecular Volume of Oxysulphobenzide. By J. ANNAHEIM (*Deut. Chem. Ges. Ber.*, ix, 1148—1150).—To obtain well defined crystals of oxysulphobenzide $(C_6H_4.OH)_2SO_2$, it is dissolved in boiling glacial acetic acid, and the nearly saturated solution placed in a water-bath, which is heated to 100° . A second larger inverted beaker is then put over it, the whole covered with a cloth, and left to itself for 24 hours. The crystals are often 2 cm. long, and 5—6 mm. thick, and belong to the orthorhombic system, being combinations of $\infty P\infty$, $\infty P\bar{2}$, $0P$, P . Axial ratio, $a : b : c = 0.53419 : 1.2829 : 1$. The specific gravity at 15° is 1.3663, corresponding with the molecular volume 182.9, which number agrees very closely with that calculated from the atomic volumes of the elements; that of amorphous carbon = 7.5; of rhombic sulphur = 15.6; of hydrogen, 6.5; and of oxygen, 5; the two latter being calculated from the molecular volume of water.

The specific gravities of the following derivatives were also determined:—

	Spec. grav.	Temp.	Mol. vol.
Tetrachoroxyulphobenzide	1.7774	16°	218.2
Tetrabromoxyulphobenzide	2.3775	17°	238.0
Tetraiodoxyulphobenzide	2.7966	19°	269.5

C. S.

Two Benzenedisulphonic Acids and their Relations. By W. KOERNER and G. MONSELISE (*Gazzetta chimica italiana*, vi, 133—142).—Most chemists now consider the relation between the dihydroxyl and dicarboxyl derivatives of benzene to be that represented by the formulæ—



One of the greatest difficulties in the acceptance of this hypothesis is the fact that the benzenedisulphonic acid discovered by Hofmann and Buckton yields both resorcin and terephthalic acid. It seemed not impossible, however, that the disulphonic acid hitherto considered as homogeneous, was really a mixture of two isomeric acids, $C_6(SO_3H)H(SO_3H)H_3$ and $C_6(SO_3H)H_2(SO_3H)H_2$. This supposition has been fully confirmed by experimental evidence.

The benzenedisulphonic acid was prepared by dissolving two parts of pure benzene in three parts of a mixture of ordinary (1 vol.) and fuming (2 vols.) sulphuric acid, and heating the product with three-fourths its volume of the fuming acid to 200—245° for 3—5 hours. The black mass was then dissolved in water and neutralised with calcium carbonate, the calcium salt was converted into the potassium salt, and the solution evaporated. By this means crystals of two kinds were obtained, which had to be separated mechanically. One of these, *potassium α -benzenedisulphonate*, $C_6(SO_3K)H(SO_3K)H_3 + H_2O$, corresponding with isophthalic acid, forms large, colourless, sharply-defined prisms, very soluble in water, but insoluble in alcohol; whilst the other, *potassium β -benzenedisulphonate*, $C_6(SO_3K)H_2(SO_3K)H_2 + H_2O$, corresponding with terephthalic acid, was obtained in ill-defined, thin, iridescent plates, less soluble in water than the α -compound. The acids were liberated from the purified potassium salts by adding a considerable excess of sulphuric acid, precipitating the potassium sulphate by alcohol, and finally removing the excess of sulphuric acid with barium hydrate. Both acids are deliquescent, crystalline substances, closely resembling each other.

Derivatives of α -Benzenedisulphonic Acid.—The *barium-salt*, $C_6(SO_3)H(SO_3)H_3 + 2H_2O$, crystallises from a dilute solution in large,

Ba

colourless prisms, which are sometimes quite transparent, whilst from a concentrated solution it separates in nodules consisting of colourless needles. The *lead salt*, $C_6(SO_3)H(SO_3)H_3 + 2H_2O$, appears to be

Pb

isomorphous with the barium salt. The *copper salt*, $C_6(SO_3)H(SO_3)H_3$

Cu

+ $6H_2O$, forms blue needles; the *sodium salt*, $C_6(SO_3Na)H(SO_3Na)H_3 + 4H_2O$, crystallises in colourless needles, and the *cadmium salt* in small, colourless prisms.

α-Dicyanobenzene, $C_6(CN)H(CN)H_3$, is obtained, together with ammonium carbonate, by distilling a mixture of the potassium *α*-disulphonate with potassium cyanide. It is readily purified by washing with water and crystallisation from alcohol, in which it is very soluble. It forms needles, which melt at 156° . It is readily decomposed by boiling with potassium hydrate solution, yielding potassium isophthalate, with evolution of ammonia. The isophthalic acid melts above 320° , and yields the characteristic soluble barium salt.

α-Benzenedisulphonic chloride, $C_6(SO_2Cl)H(SO_2Cl)H_3$, formed by the action of phosphorus perchloride on the potassium salt of the *α*-acid, crystallises from ether in large, colourless prisms, which melt at 63° ; it is converted into the corresponding *amide*, $C_6(SO_2NH_2)H(SO_2NH_2)H_3$, by the action of ammonia-solution. The amide crystallises in needles, resembling sublimed benzoic acid, and melts at 229° .

Thioresorcin is formed by the reducing action of tin and hydrochloric acid on the chloride, and after being purified by distillation in a current of steam, forms a crystalline mass of aromatic odour, resembling that of the leaves of some species of geranium. It melts at 27.1° , and distils unaltered at 245° . It readily yields metallic derivatives.

Derivatives of β-Benzenedisulphonic Acid.—The *barium salt*, $C_6(SO_3)H_2(SO_3)H_2 + H_2O$, forms crystalline crusts, consisting of

Ba

microscopic needles, much less soluble in water than the corresponding *α*-compound. The *lead salt*, $C_6(SO_3)H_2(SO_3)H_2 + H_2O$, forms small,

Pb

granular crystals, which under the microscope are resolved into nodules of minute needles. This also is somewhat less soluble than the *α*-compound.

β-Dicyanobenzene is readily prepared in a manner similar to the *α*-compound, the yield being considerably greater. It crystallises in large lustrous needles, which melt at 222° , but begin to sublime at 153° . It is very slightly soluble in alcohol, even when boiling, and is deposited again almost entirely when the solution is cold. By the action of a boiling solution of potassium hydrate, the cyanobenzene is converted quantitatively into terephthalic acid.

β-Benzenedisulphonic chloride, $C_6(SO_2Cl)H_2(SO_2Cl)H_2$. The action of phosphorus perchloride on the *β*-disulphonate, is much less violent than with the *α*-compound, the product being obtained at once in the crystalline state. It is less soluble in ether than the *α*-dicyanobenzene, crystallising in long, transparent needles which melt at 131° . The *amide*, $C_6(SO_2NH_2)H_2(SO_2NH_2)H_2$, crystallises from water in very thin scales, and from alcohol in small plates which melt at 288° .

Thiohydroquinone is formed from *β*-benzenedisulphonic chloride by the action of tin and hydrochloric acid, subliming in lustrous, hexagonal plates. It is purified by distillation in a current of steam, and crystallisation from boiling alcohol, in which it is but slightly soluble. The colourless crystals become oxidised on exposure to the air, with formation of a yellow powder. Thiohydroquinone melts at 98° , and possesses an aromatic odour, distantly resembling that of the *tropaeolum*.

It yields metallic derivatives, the lead compound being an orange-red precipitate, which is unaltered by a concentrated solution of potassium hydrate, even when heated with it at 200° for several hours.

C. E. G.

Sulphoparachlorobenzoic Acid. By TH. CÖLLEN and C. BÖTINGER (*Deut. Chem. Ges. Ber.*, ix, 1247—1251).—The preparation and properties of this acid and some of its salts were described in a former paper (see this Journal, 1876, ii, 412). Some other compounds have now been examined.

The *acid sodium salt* crystallises in tufts of needles, which contain 2 mol. of water, and are easily soluble in water. The *magnesium salt* forms needles containing 6 mol. of water, which is given off at 150° . The anhydrous salt absorbs moisture with avidity. The *zinc salt* is very soluble, and crystallises from concentrated solutions in long shining needles containing 4 mol. of water. The *neutral silver salt* forms brilliant pointed needles containing 1 mol. of water, which it gives off at 120° , the salt decomposing at a somewhat higher temperature. It dissolves in water.

The potassium salt is not converted into dioxybenzoate by fusion with potash. When fused with potassium formate, it yields benzoic, isophthalic, and terephthalic acids.

The free acid, when treated with sodium-amalgam, is deprived of chlorine, and at the same time reduced. No definite products of the reaction have been obtained.

Phosphorus pentachloride, acting on the acid, forms a chloride, which crystallises from ether in long needles melting at 150° , and agrees in composition with the formula $C_6H_3Cl.CO.SO_2.OH.Cl$. This body, when dissolved in alcohol, is converted into the *ethyl-compound*, $C_6H_3Cl.CO.SO_2.OHOC_2H_5$, which forms long needles melting about 150° . The chloride, when treated with alcoholic ammonia, yields the ammonium salt of the *amide*, $C_6H_3Cl.CO.SO_2.ONH_4.NH_2$, which crystallises in hair-like needles, melting at about 230° . J. R.

Sulphoparabromobenzoic Acid. By C. BÖTINGER (*Deut. Chem. Ges. Ber.*, ix, 1251).—In a previous paper, the author stated that this acid yields a chloride melting at 155° , with decomposition. Further examination of the reaction has shown that various monochlorides are formed according to the temperature. The chloride formed in the cold (that previously described as above) melts at 176° , and is converted at a higher temperature into another chloride melting at 108° . The former of these is designated α -chloride, the latter β -chloride.

The α -chloride has an acid reaction. The *ethyl-compound* melts at 165° . The *amide* melts at 252 — 254° , and crystallises in long needles: its ammonium salt melts at 203° .

The β -chloride forms an *ethyl-compound* melting at 90° , and crystallising in laminæ which sublime undecomposed. The *amide* melts at 229 — 230° , and forms an ammonium salt crystallising in needles and melting at 125 — 126° . J. R.

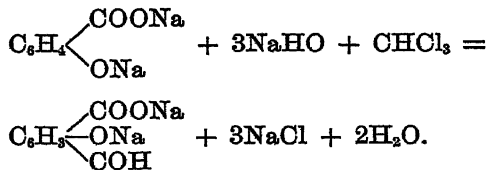
Action of Chloroform on Aromatic Oxy-acids in Alkaline Solution. By K. REIMER and FERD. TIEMANN (*Deut. Chem. Ges. Ber.*, ix, 1268—1278).—**SALICYLIC ACID.**—When pure salicylic acid (14 parts) and solid sodium hydrate (25 parts), dissolved in water (50 parts) are boiled with chloroform (15 parts) for some hours, and the product of the reaction is dissolved in water and strongly acidified with hydrochloric acid, a yellow precipitate is thrown down, which dissolves readily in ether, and is taken up therefrom almost entirely by an aqueous solution of acid sodium sulphite. The latter solution, when boiled with dilute sulphuric acid, deposits a crystalline precipitate, separable by crystallisation from water into the two following bodies:—

1. *Paraldehydosalicylic acid*, C_6H_5 $\begin{matrix} \diagup COOH \\ \diagdown OH \\ \diagdown COH \end{matrix}$.—This substance crystal-

lises first in long delicate yellowish needles, melting when pure at 248—249°, and dissolving freely in ether and hot alcohol, but very sparingly in water and chloroform. The aqueous solution produces a deep cherry-red coloration with ferric chloride. It decomposes carbonates with effervescence, and combines with acid sodium sulphite, thus behaving both as an acid and an aldehyde, whence it appears that it is formed by the introduction of the aldehyde-group into salicylic acid. Its calcium salt, when submitted to dry distillation with calcium hydrate, yields paraoxybenzoic acid. The author concludes, therefore, that the aldehyde-group occupies the para-position in relation to the hydroxyl.

2. *Orthoaldehydosalicylic acid.*—This body is contained in the mother-liquor of the preceding, and is taken up therefrom by ether, which leaves it on evaporation in the form of a white crystalline mass. When pure, it crystallises in delicate needles, which melt at 166°, and sublime without decomposition at a somewhat higher temperature. Its aqueous solution is coloured yellow by soda, and red by ferric chloride. It decomposes carbonates with effervescence, and combines with acid sodium sulphite, like the preceding compound, with which it is isomeric. Its calcium salt, when distilled with calcium hydrate, yields pure salicylic aldehyde, whence it is concluded that the aldehyde-group occupies the ortho-position in relation to the hydroxyl.

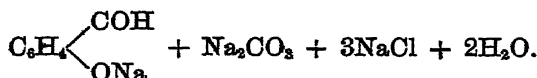
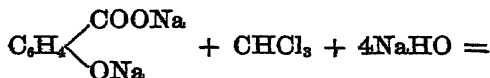
The formation of the foregoing compounds is represented by the equation—



PARAOXYBENZOIC ACID.—This acid, when treated with sodium hydrate and chloroform, in the same manner as salicylic acid (see above), yields the two following products:—

1. *Orthoaldehydo-oxydracrylic acid*, C_6H_3 $\begin{matrix} \diagup COOH \\ | OH \\ \diagdown COH \end{matrix}$.—A substance crystallising in thin yellow prisms, which melt at $243-244^\circ$, and sublime in long white needles at a somewhat higher temperature. It dissolves sparingly in chloroform and water, easily in alcohol and ether. The aqueous solution is coloured an intense yellow by soda, and brick-red by ferric chloride. It decomposes carbonates with effervescence, and combines with acid sodium sulphite, and must, therefore, be regarded as an aldehydo-oxybenzoic acid. Its calcium salt, when submitted to dry distillation, yields salicylic aldehyde, and a small quantity of phenol, showing that the aldehyde residue and the hydroxyl-group occupy the same positions as in salicylic aldehyde. Hence the above name.

2. *Paraoxybenzaldehyde*, C_6H_4 $\begin{matrix} \diagup COH \\ | OH \end{matrix}$.—This substance, which is separated from the preceding with difficulty, melts at $115-116^\circ$. Its aqueous solution has an acid reaction, and gives with ferric chloride a faint bluish-violet coloration. Its formation from paraoxybenzoic acid is represented by the equation—



J. R.

Rufigallic Acid. By W. KLOBUKOWSKI (*Deut. Chem. Ges. Ber.*, ix, 1256—1262).—The author has continued his experiments on the reactions of this acid. (For an abstract of a previous paper, see this Journal, 1876, i, 259).

Rufigallic acid dissolves in cooled fuming nitric acid, and in weaker acid on warming, evolving large quantities of gas—chiefly carbon dioxide. The solution yields oxalic acid when evaporated.

Fuming sulphuric acid dissolves rufigallic acid with dark purple-red colour, and deposits it unaltered on dilution. The solution evolves sulphur dioxide when heated. Sulphuric anhydride, mixed with the acid, converts it into a thick violet-coloured pulp, from which the acid is recovered unchanged on addition of water.

Bromine and phosphorus pentachloride both act on rufigallic acid, but no definite products of the reaction have been obtained.

Rufigallic acid submitted to dry distillation with lime or baryta is mostly carbonised, a slight sublimate only, apparently of naphthalene, being formed, and an inflammable gas evolved.

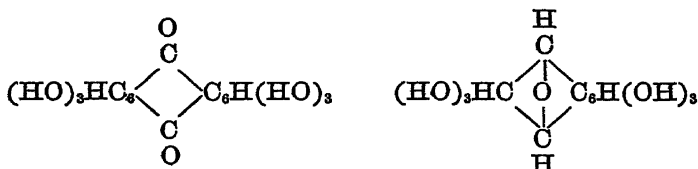
Rufigallic acid, heated with hydriodic acid and phosphorus, yields a yellow crystalline body, the composition of which agrees with the formula, $C_{14}H_{10}O_7$. This substance is not soluble without decomposition. Distilled with zinc-dust, it yields anthracene. When heated

with acetic anhydride, it is converted into a crystalline compound, agreeing in composition with the formula—

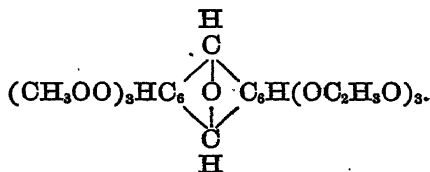


The action of hydriodic acid on rufigallic acid, $\text{C}_{14}\text{H}_8\text{O}_6$, is therefore to replace an atom of oxygen by two atoms of hydrogen.

Now, if rufigallic be regarded as a body formed from two substituted benzene-nuclei united by two CO-groups, the acid and the reduction-product may be represented thus:



and the acetyl-compound thus:



These formulæ, however, are based on the assumption that the acid is capable of taking up six acetyl-groups, the presence of which has not yet been demonstrated experimentally in the acetyl-compounds of either the acid or the reduction-product.

J. R.

Action of Phosphorus Pentachloride on Nitronaphthalenes. By ALBERT ATTERBERG (*Deut. Chem. Ges. Ber.*, ix, 1187—1189).—Nitrochloronaphthalene melting at 85° , when heated with an equivalent quantity of phosphorus pentachloride, yields a dichloronaphthalene which crystallises in long brittle needles melting at 66° , and is identical in properties with the β -dichloronaphthalene of Faust and Saame.

Nitro- γ -dichloronaphthalene, similarly treated, yields a trichloronaphthalene crystallising in long colourless needles, which melt at 129° . This product is not identical with any of the known trichloronaphthalenes, all of which melt at lower temperatures.

α -Dinitrochloronaphthalene melting at 106° is only partially acted on by phosphorus pentachloride, the product being a trichloronaphthalene, apparently identical with that just mentioned.

α -Dinitronaphthalene, heated to 217° with phosphorus pentachloride, yields a chloronaphthalene which crystallises in fine laminæ melting at 107° , and is identical in properties with the γ -dichloronaphthalene previously described by the author.

β -Dinitronaphthalene, heated to 170° with phosphorus pentachloride,

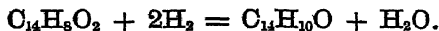
yields a trichloronaphthalene melting at 129°, and identical with that obtained from nitro- γ -dichloronaphthalene and α -dinitrochloronaphthalene (see above).

α -Nitronaphthol, when heated with phosphorus pentachloride, yields a small quantity of β -dichloronaphthalene melting at 67°. Hence β -dichloronaphthalene, α -nitronaphthol, and nitrochloronaphthalene are corresponding and similarly constituted bodies. Naphthoquinone must also belong to the same series, Liebermann having obtained it from α -nitronaphthol. J. R.

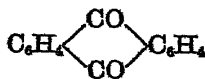
An Isomeride of Dibromanthracene. By OSWALD MILLER (*Liebig's Annalen*, clxxxii, 366).—Dibromanthraquinone, when heated to 150° with hydriodic acid and red phosphorus, yields by reduction a substance isomeric with dibromanthracene. The new body is extracted from the products of the reaction by benzene. It crystallises from alcohol in brilliant golden-yellow rectangular tables, which melt at 190—192°. It dissolves sparingly in alcohol and benzene. Strong sulphuric acid dissolves it easily, forming a reddish-brown solution, from which water throws down unaltered dibromanthracene. By oxidation it is converted into dibromanthraquinone. The investigation is being continued. J. R.

Anthranol. By C. LIEBERMANN and TOPF (*Deut. Chem. Ges. Ber.*, ix, 1201—1203).—Anthraquinone, when treated with hydriodic acid and phosphorus in excess, yields anthracene dihydride, $C_{14}H_{12}$, which may thus be obtained with ease in large quantities. It crystallises from alcohol in large laminæ melting at 108°.

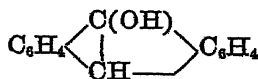
But when the reducing action is allowed to proceed for a short time only, the product is a body intermediate in composition between anthraquinone and anthracene dihydride. This substance, called *anthranol* by the authors, crystallises from alcohol in yellow needles. Its formation is represented by the equation—



Anthranol forms with acetic anhydride yellow needles of a monacetyl-compound, $C_{14}H_8(C_2H_3O)O$, melting at 126—131°; whence the authors conclude that, if the constitution of anthraquinone be represented by the first of the following formulæ, that of the new substance must be expressed by the second:



Anthraquinone.



Anthranol.

Anthranol is reduced to anthracene by zinc-dust at a red-heat, and is oxidised to anthraquinone by nitric or chromic acid. Fuming nitric acid in the cold converts it into a nitro-compound crystallising in needles. It does not dissolve completely in alkalis: on prolonged boiling of the solutions, it is partially converted into anthraquinone.

It melts at temperatures varying between 163° and 170° , and at higher temperatures turns green and carbonises without volatilising.

J. R.

Xanthopurpurin. By H. PLATH (*Deut. Chem. Ges. Ber.*, ix, 1204—1206).—Xanthopurpurin is best obtained by the reduction of purpurin with stannous chloride in alkaline solution. It sublimes when pure in yellowish-red needles which melt at 262° . It crystallises from glacial acetic acid in brilliant short needles.

Xanthopurpurin forms crystalline *sodium*, *barium*, and *calcium salts*, the last named crystallising in dark reddish-brown needles which agree in composition with the formula $C_{14}H_6(O_2Ca)_3O_3$.

Dimethylxanthopurpurin, $C_{14}H_6(CH_3O)_2O_2$.—This substance is obtained by heating to 120° a mixture of xanthopurpurin, methyl iodide, and potash, in molecular proportions. The product crystallises from glacial acetic acid in small pale-yellow needles melting at 178 — 180° .

Diethylxanthopurpurin, $C_{14}H_6(C_2H_5O)_2O_2$, obtained in the same manner as the preceding compound, forms yellow needles easily soluble in alcohol and glacial acetic acid, but insoluble in water. It melts at 170° .

Dibromoxanthopurpurin, $C_{14}H_6Br_2O_4$, is formed by the direct action of bromine on xanthopurpurin. It crystallises from glacial acetic acid in orange needles melting at 227 — 230° . Its *ammonium-compound*, $C_{14}H_6Br_2(O.NH_4)_2O_2$, formed by boiling it with a solution of ammonium acetate, crystallises in red matted needles having a fine metallic lustre.

Dinitroxanthopurpurin, $C_{14}H_6(NO_2)_2O_4$, is formed by the action of nitric acid of sp. gr. 1.48 on xanthopurpurin in the cold. It dissolves in water, ether, alcohol, and glacial acetic acid, and crystallises from the last in bright-red needles, melting at 249° . The *barium-compound*, $C_{14}H_4(NO_2)_2(O_2Ba)_2O_2$, formed on adding baryta-water in excess to an aqueous solution of dinitroxanthopurpurin, crystallises in dark-red needles. The *ammonium-compound*, $C_{14}H_4(NO_2)_2(OH)(O.NH_4)O_2$, is obtained in bright-yellow silky needles by dissolving the nitro-compound in a boiling solution of ammonium acetate.

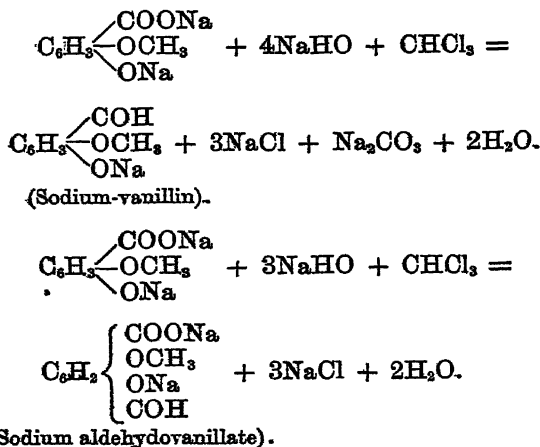
When xanthopurpurin is dissolved in strong sulphuric acid, and nitrous acid is passed into the solution, a substance is formed which crystallises from glacial acetic acid in steel-blue needles, appearing reddish by transmitted light. This substance dissolves easily in water, ether, and other solvents, melts at 249° , and has the composition of dinitroxanthopurpurin; but whether it is identical or only isomeric with the compound described above is not yet made out.

J. R.

Constitution of Compounds of the Coniferyl and Vanillin Series. By FERD. TIEMANN and B. MENDELSON (*Deut. Chem. Ges. Ber.*, ix, 1278—1284).—When 1 mol. of vanillic acid is boiled for some hours with 1 mol. of chloroform and an aqueous solution of 5 mol. of sodium hydrate, and the product of the reaction is dissolved in water and acidified with hydrochloric acid, a sparingly soluble body is thrown down, which proves on examination to be *aldehydovanillic acid*, whilst vanillin remains in solution.

The former product dissolves in ether and is taken up from the solution by acid sodium sulphite. It crystallises from boiling water in yellow silky needles, melting at 221—222°, dissolves easily in alcohol and ether, and decomposes carbonates with effervescence.

The reactions by which these products are formed may be represented thus:



This behaviour of vanillic acid is perfectly analogous to that of paraoxybenzoic acid under the same circumstances, whence the authors conclude that in the molecule of vanillic acid the carboxyl-group occupies the para-position in relation to the hydroxyl; and accordingly vanillic acid is to be regarded as metamethoxyl-paraoxybenzoic acid, and vanillin as metamethoxyl-paraoxybenzaldehyde. Aldehydovanillic acid must, for the same reason, be regarded as a derivative of salicylic aldehyde, and in fact it exhibits the characteristic behaviour of such derivatives, giving an intense yellow solution with soda, and a distinct reddish-violet coloration with ferric chloride. J. R.

The Constitution of Veratric Acid and Veratrol. By G. KOERNER (*Gazzetta chimica italiana*, vi, 142—148).—It was found that veratric acid yielded protocatechuic acid when submitted to the action of fused potassium hydrate, a result in accordance with the author's idea that this rare acid was a trisubstitution derivative of benzene, resembling anisic acid. He was thus induced to study the action of hydriodic acid on veratric acid, and found that when the two were heated together for some time at 150—160°, methyl iodide was formed together with protocatechuic acid (m. p. 199°), and a small quantity of another acid which, again heated with hydriodic acid at 170°, yielded methyl iodide, carbonic anhydride, and pyrocatechin. This result distinctly proved that veratric acid is identical with dimethylprotocatechuic acid, but in order to obtain additional evidence, the author prepared dimethylprotocatechuic acid synthetically. Pure protocatechuic acid (from essence of cloves) was converted into methylic dimethylprotocatechuic acid by treating it with sodium methylate and

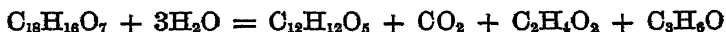
methyl iodide. The ether when pure crystallises in colourless needles, melting at 58° , and possessing an agreeable, although feeble, aromatic odour. It is easily saponified by treatment with solution of potassium hydrate, and the solution, on the addition of hydrochloric acid, deposits the dimethylprotocatechuic acid in needles which have the same melting point as veratric acid, namely, 179.5° , and is identical with the latter in all its properties. Veratric acid is therefore closely allied to vanillin, being identical with methyl-vanillic acid, the formulæ, $C_6(OCH_3)(OCH_3)H(COOH)H_2$, and $C_6(OCH_3)(OCH_3)H_4$, representing veratric acid and veratrol respectively.

The author thinks that the different results obtained by Koelle (*Ann. Chem. Pharm.*, clix, 240) are probably due to his dimethylprotocatechuic acid being contaminated with a small quantity of monomethylprotocatechuic acid.

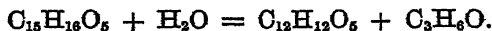
C. E. G.

Usnic Acid. By E. PATERNÒ (*Gazzetta chimica italiana*, vi, 113—133).—The research described in this paper has already been briefly noticed (this Journal, 1876, vi, 202, and *Deut. Chem. Ges. Ber.*, ix, 345). The memoir commences with an historical summary, after which the method of preparation of the acid from *Zeora sordida* is fully described and its principal reactions given. Treated with sulphuric acid and potassium dichromate, it yields acetic acid. Acetyl chloride has no action on usnic acid, even when boiled with it, whilst at 100° in sealed tubes the acid is converted into carbonaceous products. *Decarbusnic acid*, $C_{15}H_{16}O_5$, is formed not only by the action of ethyl alcohol at 150° on usnic acid, but also by the action of methyl alcohol and allyl alcohol. Water also acts in the same manner, but very slowly, owing probably to the slight solubility of the acid in it.

Amongst the products of the action of a solution of potassium hydrate on usnic acid, the author has verified the presence of carbonic anhydride, acetic acid and acetone, so that the equation—



really represents the formation of pyrousnic acid, $C_{12}H_{12}O_5$, from usnic acid, $C_{18}H_{16}O_7$. It is not improbable that decarbusnic acid is formed as an intermediate product which becomes transformed into pyrousnic acid, thus—



The formation of acetone renders it highly probable that usnic acid, and perhaps decarbusnic acid, contains the group $C(CH_3)_2$.

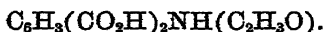
When pyrousnic acid is heated it decomposes, yielding a crystalline sublimate which melts at 175° ; but in order to obtain a satisfactory result, the operation should be conducted in a current of hydrogen: the residue left is then very small. This new substance, which not only melts 20° lower than pyrousnic acid, but is also much less soluble in water, appears to be formed without elimination of water. Its solution in potash absorbs oxygen from the air and becomes green.

If usnic acid be treated with potassium hydrate in a manner similar to that for the preparation of pyrousnic acid, but instead of boiling the solution, it be merely heated to 100° , acetone is produced, and on

adding hydrochloric acid to the alkaline solution, a yellow flocculent precipitate is obtained. This, after being purified by washing with ether and crystallisation from alcohol, is obtained in colourless micaceous plates quite different from decarbusnic acid, and from pyrousnic acid. It is but slightly soluble in water, and its alkaline solution alters readily in contact with the air, but does not turn green. It melts at a lower temperature than pyrousnic acid, and when heated in a current of hydrogen, yields a crystalline sublimate melting at about 160° , the alkaline solution of which does not become green on exposure to the air. The memoir concludes with some criticisms on Salkowski's paper on usnic acid. C. E. G.

Ethyl Santonate. By F. SESTINI (*Gazzetta chimica italiana*, vi, 148—150).—This compound is most conveniently prepared by heating silver santonate with excess of ethyl iodide, distilling off the excess of iodide, and extracting the residue with ether. On the evaporation of the ether, the ethyl santonate is left in large prisms. It may also be prepared by saturating an alcoholic solution of santonic acid with hydrochloric acid, and heating, but is then difficult to purify. The ether, which has the composition $C_{15}H_{19}(C_2H_5)_2O_4$, melts at $88-89^{\circ}$. It is readily decomposed by boiling with a dilute solution of sodium hydrate, with formation of sodium santonate; also by prolonged contact with nitric acid, santonic acid being liberated. C. E. G.

Oxidation of Aromatic Acetamines by Potassium Permanganate. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, ix, 1299—1303).—When a concentrated solution of potassium permanganate is added to a hot aqueous solution of the acetoxylide melting at $127-128^{\circ}$, a product is formed which appears to be a mixture of at least two acids. One of these, which can easily be isolated, as it forms an insoluble blue copper salt, is *acetamidophthalic acid*,

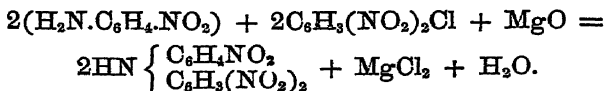


It is very sparingly soluble in water, more freely in alcohol, and separates from dilute alcohol in small white crystals melting with decomposition at $270-280^{\circ}$. The acetyl-group is not removed by heating with hydrochloric acid to 120° , whereas at 200° carbon dioxide is given off, and, probably, an amidobenzoic acid, and perhaps also aniline is formed.

Acetoparatoluide yields with potassium permanganate an acetamido-benzoic acid, which crystallises from alcohol in needles, melting with partial decomposition at 250° , and easily converted by boiling hydrochloric acid into the hydrochloride of paramidobenzoic acid.

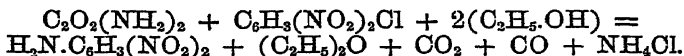
C. S.

Action of α -Dinitrochlorobenzene on Amido-compounds. By WILLGERODT (*Deut. Chem. Ges. Ber.*, ix, 1178—1181).—While aniline acts already in the cold on α -dinitrochlorobenzene, metanitriline does not even at 150° ; but on heating an alcoholic solution with magnesia to 200° the following reaction takes place:—

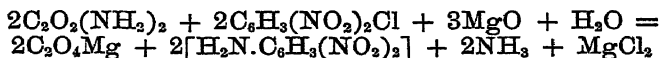


The α -dinitrophenylmetanitriline thus formed is sparingly soluble in boiling alcohol, and less so in water, ether, dilute hydrochloric acid, and dilute potash, but freely in boiling acetic acid, from which it crystallises in short, yellow needles.

When α -dinitrochlorobenzene is heated with oxamide and alcohol for six hours to 200–230°, dinitraniline is formed :



But when magnesia is added the reaction takes place at 150° and requires only two hours :



C. S.

Aniline-black. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, ix, 1168–1170).—When aniline is heated with aniline-black, a blue colouring matter is formed, which is obtained pure by boiling out the crude black with alcohol, and treating the residue with soda to obtain the base, which is converted into the acetate by moistening it with acetic acid. The dry acetate is then heated with 8–10 times its weight of aniline to 160–180° for 6–8 days. The product is then treated with an excess of dilute hydrochloric acid, which does not dissolve the hydrochloride of the new base. The latter was obtained in the free state by the action of soda and purified by dissolving in ether, precipitating this solution with hydrochloric acid, and repeating this process. The free base, which has either the formula $\text{C}_{36}\text{H}_{33}\text{N}_5$ or $\text{C}_{36}\text{H}_{31}\text{N}_5$, but probably the former, dissolves in ether with a magenta-red colour.

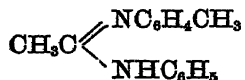
$\text{C}_{36}\text{H}_{34}\text{N}_5.\text{ClH}$ crystallises from hot alcohol in needles having a coppery lustre, while, by precipitating the ethereal solution of the base with hydrochloric acid, it is obtained as a crystalline violet powder with little lustre.

$\text{C}_{36}\text{H}_{33}\text{N}_5.\text{IH}$ is a very similar compound, and $\text{C}_{26}\text{H}_{33}\text{N}_5.\text{C}_6\text{H}_3(\text{NO}_2)_3\text{O}$ is obtained as a crystalline precipitate by adding an aqueous solution of picric acid to an alcoholic solution of the hydrochloride. $(\text{C}_{36}\text{H}_{33}\text{N}_5.\text{ClH})_2.\text{PtCl}_4$ is a violet crystalline precipitate which is sparingly soluble in alcohol and insoluble in water.

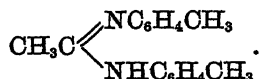
C. S.

Action of Phosphorus Pentachloride on Acetotoluidide. By O. WALLACH (*Deut. Chem. Ges. Ber.*, ix, 1214).—Amongst the products of this reaction is the imido-chloride $\text{CH}_3\text{CClNC}_6\text{H}_4\text{CH}_3$, a crystalline, easily decomposable substance, yielding with aniline, toluidine, and naphthylamine the following amidines :—

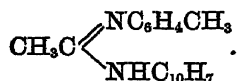
Ethenylphenyltolylamidine. White needles, melting at 86–88°—



Ethenylditolylamidine, a crystalline substance melting at 117—118°—



Ethenylnaphthyltolylamidine, a body not yet obtained in definite form—



The imido-chloride when heated evolves hydrogen chloride, and yields the hydrochloride of a base, $\text{C}_{18}\text{H}_{19}\text{ClN}_2$, which melts at 71—72°, and decomposes at 130°, the hydrochloride of a new base being formed. J. R.

Xylidines. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, ix, 1292—1299).—The author has isolated, from the crude oils of high boiling point obtained in the manufacture of aniline, a xylidine which forms sparingly soluble salts with nitric and hydrochloric acids. This he calls provisionally α -xylidine, to distinguish it from an isomeride occurring together with it (β -xylidine), which forms a sparingly soluble nitrate, but an easily soluble hydrochloride. The two isomerides were separated by repeatedly crystallising from hot water the mixture of acetyl-compounds obtained by boiling them with glacial acetic acid: the α -compound, being the less soluble, was thus obtained pure.

α -Acetoxylidide forms large flat white needles, which melt at 127—128°, and dissolve easily in alcohol. When boiled with strong hydrochloric acid, it is converted into xylidine hydrochloride. The base separated from this salt is an oil, colourless at first, but rapidly turning dark: its boiling-point is 212°, and its sp. gr. 0.9184 at 25°. Analysis of the platinum salt agrees with the formula $[\text{C}_6\text{H}_3(\text{CH}_3)_2\text{HCl}]_2\text{PtCl}_4$.

A xylidine having the same properties as the foregoing is obtained by the action of methyl alcohol on toluidine hydrochloride at 300°.

The following derivatives of α -xylidine have been prepared.

Diethylsulphocarbamide, $\text{CS}[\text{NH}\cdot\text{C}_6\text{H}_3(\text{CH}_3)_2]_2$, was obtained by digesting xylidine with carbon bisulphide till hydrogen sulphide ceased to be evolved. It is insoluble in water, and but sparingly soluble in boiling alcohol, from which it is deposited in dazzling-white hard crystals melting at 152—153°.

Xylidyl sulphocyanate is formed by distilling the preceding compound with phosphoric anhydride. It is solid at the ordinary temperature, but melts very easily.

Diethylguanidine, $\text{CNH}[\text{NH}\cdot\text{C}_6\text{H}_3(\text{CH}_3)_2]_2$, is readily formed by the action of lead oxide on xylidylsulphocarbamide in presence of alcoholic ammonia. It crystallises from hot alcohol in delicate white needles, which melt at 156—158°, apparently undergoing decomposition. It is insoluble in water.

Nitracetoxylidide, $\text{C}_6\text{H}_3(\text{CH}_3)_2(\text{NO}_2)\text{NH}(\text{C}_2\text{H}_5\text{O})$, formed by the action of strong nitric acid on acetoxylidide, crystallises from hot water or alcohol in yellow needles melting at 172—173°.

Nitroxylidine (Nitramidoxylene), $C_6H_2(CH_3)_2(NO_2)NH_2$, is formed by boiling the last compound with strong hydrochloric acid till the liquid acquires a deep-red colour. It crystallises from hot water in fine orange-red needles melting at 69° , and dissolving sparingly in water and more freely in alcohol. It is only very slowly attacked by boiling soda-ley.

Xylene-diamine (Diamidoxylene), $C_6H_2(CH_3)_2(NH_2)_2$, is formed by the action of tin and hydrochloric acid on nitroxylidine. It forms glittering laminæ or delicate white needles, which melt at $74-75^\circ$. It is a faintly alkaline base, and forms crystallisable salts. J. R.

Fluorescence of Quinidine Sulphate. By E. SCHÄER (*Deut. Chem. Ges. Ber.*, ix, 1314).—A solution of Pasteur's quinidine sulphate (Hesse's conquinine) in chloroform, after standing in the diffused light for some months, assumed a splendid green fluorescence, resembling that of certain uranium-salts. C. S.

A Homologue of Caffeine. By L. PHILIPS (*Deut. Chem. Ges. Ber.*, ix, 1308—1310).—When theobromine-silver is heated with ethyl-iodide, *ethyl-theobromine* $C_7H_7(C_2H_5)N_4O_2$ is formed, which separates from alcohol in white prismatic crystals, which are somewhat freely soluble in boiling water. It is a weak base, forming with nitric acid and hydrochloric acid crystallised salts. Its aqueous solution gives with silver nitrate a precipitate $C_7H_6Ag(C_2H_5)N_4O_2$. Ethyl-theobromine melts above 270° , and sublimes without decomposition. With chlorine-water and ammonia it gives the same reactions as caffeine.

C. S.

On Atropine. By F. SELMI (*Gazzetta chimica italiana*, vi, 153—156).—*Simplified Method of Extracting the Poisonous Alkaloids*.—The alcoholic extract of the viscera acidified and filtered is evaporated at 65° ; the residue taken up with water, filtered to separate fatty matters, and decolorised by means of basic acetate of lead, leaving the solution in contact with the air for 24 hours. It is then filtered, the lead precipitated with sulphuretted hydrogen, and the solution, after concentration, repeatedly extracted with ether. The ethereal solution is then saturated with dry carbonic anhydride, which generally causes a precipitate of minute drops, adhering to the sides of the vessel and containing some of the alkaloids. The ethereal solution is then poured into a clean vessel, mixed with about half its volume of water, and a current of carbonic anhydride passed for 20 minutes, which may cause the precipitation of other alkaloids not precipitated by dry carbonic anhydride. Usually the whole of the alkaloids present in the ether are thrown down by these means, but if not, the solution is dehydrated by agitation with barium oxide, and then a solution of tartaric acid in ether added to the clear liquid, taking great care not to employ excess of acid; this throws down any alkaloid that may remain. In order to extract any alkaloids that may still remain in the viscera, they are mixed with barium hydrate and a little water, and agitated with *purified* amyl alcohol; the alkaloids may subsequently be extracted from the alcohol by agitation with very dilute sulphuric acid.

Atropine.—As atropine is readily decomposed into tropine and atropic acid, and might become altered in the process of extraction, the author studied the action of various reagents on the alkaloid. Boiled with a solution of barium hydrate in contact with the air, it gave a pleasant odour of hawthorn flowers; but no odour was observed on distilling the mixture. The residue contained tropine, which was extracted with ether. Atropine was decomposed when boiled with dilute sulphuric acid, or with a solution of tartaric acid, but no odour was developed; a substance (A) being obtained from the solution on treatment with ether, very different in its reactions from tropine. The action of ammonia on atropine yields two substances of the nature of an alkaloid; one (B) precipitable by carbonic anhydride from the ethereal solution; the other (C) not precipitable. Their reactions are as follows:—

	Tropine.	A.	B.	C.
Tannic acid.....	White	White	White	—
Iodised hydriodic acid	Brown drops	—	Brown	Brown
Platinum perchloride	Turbidity	None	None	None
Picric acid	—	Id.	Id.	Id.
Meyer's reagent.....	White	Id.	Id.	Id.
Gold chloride	Yellow	Yellow	Yellow	Yellow
Brominated hydrobromic acid....	None	—	Yellowish	Id.
Mercuric chloride	Straw yellow	White	White	White
Sodium phosphotungstate.....	—	—	Id.	Id.
Iodide of potassium and bismuth	—	Orange-yellow	Yellow	Yellow
Iodide of potassium and cadmium	White	—	White	White

From experiments made on the putrified viscera of an animal poisoned with atropine, and on the alkaloids generated by the putrefactive process in the viscera themselves, the author finds that one of those formed in the latter case, and which may be extracted by the use of amylic alcohol (although not by ether), closely resembles atropine in its action on the animal organism. Atropine may be distinctly recognised, however, by the characteristic odour of hawthorn, given off during evaporation with baryta; by the bitter taste of the ethereal extract; and by the poisonous action of the *ethereal* extract, accompanied by dilation of the pupil.

C. E. G.

Betulin. By U. HAUSMANN (*Liebig's Annalen*, clxxxii, 368—380).—The author prepares betulin as follows:—The outer bark of the birch tree, previously boiled with water and dried, is boiled for three or four hours with 20 times its weight of 90 per cent. alcohol; the extract is strained while hot, and at once mixed with alcoholic neutral lead acetate, so long as a precipitate is produced thereby. The mixture again heated to the boiling point, is filtered, and the filtrate is freed from lead by means of ammonium carbonate, and allowed to cool, whereupon it deposits a mass of crystals of impure betulin. This product is purified by treatment with ether and crystallisation from boiling alcohol.

Pure betulin forms long, thin, colourless prisms, which, when dry, present the appearance of asbestos. It is inodorous and tasteless. It melts at 258° (corr.) to a colourless liquid, which solidifies in a glassy, amorphous mass; at a somewhat higher temperature it begins to sublime in long, extremely delicate needles. When strongly heated it gives off vapours, smelling strongly of Russia leather. It is insoluble in water, sparingly soluble in cold alcohol, ether, chloroform, and benzene, but freely soluble in the hot liquids. It dissolves also in glacial acetic acid, oil of almonds, and turpentine. Its composition agrees with the formula, $C_{36}H_{50}O_3$.

Betulin is dissolved and acted on by strong sulphuric acid in the cold, and by hydrochloric and hydriodic acids when heated therewith in sealed tubes. It is attacked also by chlorine, bromine, and iodine, but as yet no definite products of these actions have been obtained.

Betulin yields by dry distillation a number of volatile products, amongst which is one of thick, oily consistence, boiling at 243° , of sp. gr., 0.951, and having the composition of an anhydride of betulin, $-C_{36}H_{36}O$.

Betulin Diacetate.—This body was obtained by heating to 125° a mixture of betulin and acetic anhydride. It crystallises in long, colourless prisms, which melt at 223° (corr.), and solidify in a crystalline mass on cooling. It dissolves easily in benzene, sparingly in alcohol and ether. Its composition agrees with the formula, $C_{40}H_{54}O_5$.

Betulinamaric Acid.—The author calls by this name a body obtained by adding betulin gradually to nitric acid of sp. gr. 1.51. The yellow liquid thus formed leaves when evaporated a residue, which, after washing with water, is pure betulinamaric acid. Dried over sulphuric acid, it has the composition represented by the formula, $C_{36}H_{42}O_{16}$, but when dried at 110° , it loses 2 mol. of water, yielding the anhydride, $C_{36}H_{42}O_{14}$. The acid and anhydride both dissolve easily in alkalis, forming bitter salts, whence the name. They are nearly insoluble in water, to which they impart a yellow colour and faint acid reaction. They dissolve in all proportions of alcohol and ether, and are soluble also in concentrated acids. The anhydride melts at 185° , undergoing decomposition.

The acid forms two classes of salts, one containing $4H_2O$ less than the other, their general formulæ being $C_{36}H_{40}O_{12}R'_4$, and $C_{36}H_{48}O_{16}R'_4$. These are regarded by the author as salts of two different acids, susceptible of transformation one into the other by elimination or assimilation of water.

The *potassium salt*, $C_{36}H_{40}O_{12}K_4$, obtained by evaporating a solution of the acid and potassium carbonate in water, exhausting the dry mass with alcohol, and evaporating, is a yellowish-brown, hygroscopic mass. From it are derived the *calcium salt*, $C_{36}H_{40}O_{12}Ca_2$; the *barium salt*, $C_{36}H_{40}O_{12}Ba_2$; the *lead salt*, $C_{36}H_{40}O_{12}Pb_2$, all yellowish-white precipitates; and the *copper salt*, $C_{36}H_{48}O_{16}Cu_2$, which is a green precipitate.

The *calcium salt*, $C_{36}H_{48}O_{16}Ca_2$, was obtained by evaporating a solution in water of the acid and calcium carbonate. The *lead salt*, $C_{36}H_{48}O_{16}Pb_2$, was precipitated by neutral lead acetate from an alcoholic solution of the acid.

When betulinamaric acid dissolved in alcohol is saturated with hydrogen chloride, and heated to 120° in sealed tubes, a compound is formed, agreeing in composition with the formula, $C_{44}H_{84}O_{14}$, which is that of the neutral ethyl ether of the acid, *minus* 2 mol. of water ($C_{36}H_{48}O_{16}(C_2H_5)_4 - 2H_2O$). It melts at 119° (corr.).

Betulinic Acid.—This acid is formed, together with resinous products, on adding chromic anhydride to a solution of betulin in glacial acetic acid, and gently warming the liquid. It forms when pure a white powder, nearly insoluble in water, but easily soluble in alcohol. It melts at 200° (corr.), and gives on analysis numbers agreeing with the formula, $C_{36}H_{54}O_6$. Its alcoholic solution gives with neutral lead acetate an amorphous precipitate, agreeing in composition with the formula, $(C_{36}H_{51}O_6)_2Pb_3$, whence it would seem that the acid is tri-basic. J. R.

Glycyrreretin. By P. WESELSKY and R. BENEDICT (*Deut. Chem. Ges. Ber.*, ix, 1158—1159).—This compound, which is formed together with sugar, by boiling glycyrrhizin with dilute acids, yields when fused with potash only *paroxybenzoic acid*. C. S.

Lignite-tar. By O. BUEG (*Deut. Chem. Ges. Ber.*, ix, 1207—1209).—The heavy high-boiling oils of lignite tar contain a substance capable of combining with picric acid, to form a compound which crystallises from benzene in long needles, and gradually decomposes in the air. When the crystals are decomposed with ammonia, and the oil thus liberated is dissolved in carbon bisulphide or chloroform, and saturated with bromine or chlorine, pale-yellow crystals of a bromine- or chlorine-compound are deposited. These compounds are insoluble in water, alcohol, ether, chloroform, carbon bisulphide, and benzene, and soluble in xylene and the high-boiling oils of coal-tar only on prolonged boiling. They are deposited from their solutions in small needles, agreeing in composition with the formula $C_{18}H_5Br_4$, or $C_{18}H_5Cl_4$.

The same compounds may be obtained by treating the crude oils directly with bromine or chlorine. They are not acted on by sodium-amalgam, or by potash. When heated with zinc-dust, they yield a hydrocarbon, crystallising in laminae, which melt at 122° , and dissolve in alcohol, glacial acetic acid, ether, chloroform, and carbon bisulphide, forming greenish-yellow fluorescent solutions. The boiling point of the hydrocarbon lies above 360° . Its formula, deduced from analysis, is $C_{18}H_{12}$.

A solution of the hydrocarbon in chloroform gives, on addition of bromine, a yellowish-white precipitate of a bromine-compound, $C_{18}H_5Br_3$, which dissolves in boiling benzene, and crystallises therefrom in small needles. The hydrocarbon is converted by oxidation with chromic acid into a quinone-like body, of reddish-brown colour, agreeing in composition with the formula, $C_{10}H_6O_2$. J. R.

Some Constituents of Adonis Vernalis. By F. LINDEROS (*Liebig's Annalen*, clxxxii, 365).—According to the author's investigation, the leaves of this plant, gathered at the time of flowering, contain

10 per cent. of their weight (when dry) of aconitic acid, in the form of calcium and potassium salts. J. R.

On the Acids in Roman Chamomile Oil. By RUDOLPH FITTIG (*Deut. Chem. Ges. Ber.*, ix, 1195).—The author has obtained from this oil an acid, melting at 45°, and boiling at 185°, and a second acid melting at 65°, and boiling at 198·5°. These acids are present in about equal proportions. Both agree in composition with the formula $C_6H_8O_2$. Besides these the oil contains another acid, boiling at 160°. The investigation is being continued. J. R.

Some Constituents of Gelsemium Sempervirens. By F. L. SONNENSCHNEIN (*Deut. Chem. Ges. Ber.*, ix, 1182—1186).—The root of this plant, which in North America is used for medical preparations, contains, according to Wormsley, a peculiar acid, which he calls *gelsemic acid*. This body is, however, identical with *æsculin*. Besides this compound, the root contains also an alkaloid, *gelsemine*, which was obtained as an amorphous, colourless, or slightly pinkish mass, melting below 100° to a colourless liquid. It dissolves but sparingly in water, more readily in alcohol, and freely in ether and chloroform. Its solution has a very bitter taste, and a strongly alkaline reaction. Its hydrochloride is amorphous, neutral, readily soluble in water, and the solution is precipitated by tannic acid, solution of iodine in potassium iodide, gold chloride, phosphomolybdic acid, &c. Platinic chloride produces an amorphous, lemon-yellow precipitate, which dissolves on warming, and crystallises on spontaneous evaporation in transparent, quadratic octohedrons, which, on the addition of water, are changed into the amorphous compound, while platinic chloride goes into solution.

The composition of gelsemine is $C_{11}H_{19}NO_2$; that of the hydrochloride $(C_{11}H_{19}NO_2)_2ClH$, and of the amorphous platinum-salt—



The pure alkaloid dissolves in concentrated nitric acid, with a greenish-yellow, and in sulphuric acid with the same colour, which, however, soon changes into a reddish-brown and dirty-red. When potassium dichromate is added to the sulphuric acid solution, the liquid changes first into cherry-red, and then into bluish-green, while by using cerosceric oxide a bright cherry-red colour is produced. On administering 0·012 gram of the hydrochloride to a large pigeon, it died with convulsions in 36 minutes, and frogs exhibited the same symptoms. C. S.

Physiological Chemistry.

Equivalent Substitution of Mineral Substances in Animals and Plants. By P. CHAMPION and H. PELLET (*Compt. rend.*, lxxxiii, 485—488).—A table of analyses of the ash from the flesh of various animals and from eggs is given to show that while there is considerable variation in the relative amounts of soda, potash, lime, and magnesia, the quantity of sulphuric acid required to saturate the whole of the bases in each case varies within narrow limits, and the quantity of phosphoric acid present in the ashes is nearly constant.

R. R.

Assimilation of different Sorts and Mixtures of Foods by Pigs. By WOLFF, FUNKE, and DITTMANN (*Landw. Versuchs-Stat.*, xix, 241—313).—This paper contains an account of some experiments carried out at the Experimental Station of Hohenheim during 1872—1873, of which the chief novelty is an enquiry into the nutritive value of cockchafers. Some of the results have already been published in the *Württemb. Wochenblatt für Land. u. Forstwirtschaft*, 1873, No. 49, and they have also been briefly noticed by Wolff in a paper read at the meeting of the German Natural Philosophers at Wiesbaden, Sept., 1873 (*Jour. Chem. Soc.*, xxvii, 384), but the publication of a complete and classified report has hitherto been unavoidably delayed.

Four young pigs of half English breed were selected, two and two from the same litters, those mentioned as Nos. 2 and 4 being about twelve weeks old, and the other two, Nos. 1 and 3, between five and six months old at the commencement of the experiments. They were fed always three times a day, their food being mixed with lukewarm water, generally in the proportion of about a liter to every 200 grams. The more important results are shown in the following tables:—

Composition of dried Feeding Materials, the Digestibility of which could be determined with tolerable accuracy.

	Protein substance.	Fat.	Fibre.	Non- nitrogenous extractive matter.	Ash.
Cockchafers	64·09	7·29	16·06	4·73	7·83
Cocoa-nut cake	26·69	8·60	13·66	44·93	6·12
Barley meal (a)	14·05	3·07	5·13	74·78	2·97
" " (b)	12·65	3·18	4·28	77·10	2·79
Indian-corn meal	10·59	4·97	2·18	80·18	2·08
Pea meal	26·03	2·12	8·67	59·78	3·40

Coefficients of Digestibility.

	Protein.	Fat.	Fibre.	Extractive matter.
Cockchafers	68·97	83·04	— *	—
Cocoa-nut cake	73·44	83·20	60·35	89·24
Barley meal (a)	78·00	65·92	18·62	90·09
" " (b)	79·11	72·28	—	91·17
Indian-corn meal	84·53	76·46	18·65	92·81
Pea meal	84·43	66·52	61·80	94·76

The amount of *actual* nourishment, *i.e.*, constituents actually digestible, contained in a hundred parts of dried food is therefore as follows:—

	Protein.	Fat.	Fibre.	Extractive matter.
Cockchafers	44·20	6·05	— *	—
Cocoa-nut cake	19·60	7·16	8·24	40·10
Barley meal (a)	10·96	2·02	0·96	67·37
" " (b)	10·01	2·30	—	70·29
Indian-corn meal	8·95	3·80	0·41	74·41
Pea meal	21·98	1·41	5·36	56·65

It will be seen that the protein substance of cockchafers and cocoa-nut cake is less digestible than that of barley meal, whilst the protein of maize and pea meal is more so; but that the fat of cockchafers and cocoa-nut cake is better digested than that of pea and barley meal, the coefficient for Indian-corn meal being about the mean.

The following table shows the daily increase in the weight of the animals, and the quantity of dry food and of actually digestible constituents required for the production of 100 kilograms of live weight:—

* Chitin is quite indigestible to pigs.

Description of Food.	Duration of Experiment.	Increase in weight per head per day.	For the production of 100 kilograms of live weight.			
			Dry food.	Albumin.	Fat.	Carbohydrates.
<i>Pigs 1 and 2.</i>	Days.	Kilos.	Kilos.	Kilos.	Kilos.	Kilos.
Barley meal	16	0·369	441	48·4	9·3	334·8
2 barley + 1 cockchafers....	16	0·393	415	90·0	13·7	194·5
1 barley + 1 cockchafers....	15	0·332	488	133·4	19·5	172·5
Barley meal	24	0·451	452	45·3	10·4	317·7
" "	28	0·495	433	42·4	9·2	304·6
" "	16	0·492	422	42·1	10·9	297·1
" "	12	0·461	450	45·4	11·6	317·0
<i>Pigs 3 and 4.</i>						
Barley meal	16	0·375	377	41·0	7·0	251·9
1 barley + 1 cocoa-nut cake..	16	0·325	437	60·2	16·2	267·0
2 barley + 1 cockchafers....	15	0·327	430	92·2	13·7	197·7
Barley meal	24	0·398	439	43·9	10·1	308·6
8 barley + 1 cockchafers....	28	0·430	394	56·2	10·1	244·0
6 barley + 1 starch	16	0·411	454	39·5	9·6	335·1
<i>Pigs 2 and 4.</i>						
3 barley + 1 starch	12	0·504	373	25·0	5·6	235·8
Maize meal	16	0·273	648	58·0	24·6	434·8
Pea meal.....	15	0·411	367	80·8	5·5	227·3

The mean of 14 of the above experiments shows an increase of 100 kilograms in weight to have been produced by the consumption of 432 kilograms of dry barley, or 358 kilograms of actually digestible organic substances.

H. H. B. S.

Formation of Pepsin in Batrachians. By H. VON SWIECICKI (*Pflüger's Archiv. f. Physiologie*, xiii, 444—452).—A microscopical examination of the stomach of the frog reveals in its cardiac end, as also in the oesophagus, peculiar glands, which have not hitherto been described, and concerning whose physiological importance nothing is known.

These glands, which stretch in thick layers from the commencement of the oesophagus to the cardiac dilatation of the stomach, present distinct differences according to the stage of digestion. They are of a ramified tubular form, possessing dull cylindrical cells, which exhibit an ordinary eccentric nucleus. Though varying in size, the cells show a clear outline, and a tendency to coloration (carmine, hæmatoxylin). Both-sized cells are found together, the larger being in excess in that portion of the membrane richest in pepsin.

Chemical experiments show that during digestion the cells are larger and contain more pepsin than during fasting; also that the quantity of pepsin in the oesophagus exceeds that of the stomach, whilst the pyloric region always contains the least. This fact led to

other experiments, which show that the formation of pepsin takes place almost entirely in the oesophagus, whilst the cells of the stomach form the acid.

The quantity of pepsin formed increases during the first 6 to 10 hours of digestion, then decreases until about the 20th hour, when it attains its minimum, and again increases.

These results have been verified upon other batrachians.

F. J. L.

Acetone in Urine. By W. MARKOWNIKOFF (*Liebig's Annalen*, clxxxii, 362—364).—The author found in 73 liters of the urine of a boy of 16, suffering from diabetes complicated with other disorders, 30 grams of acetone and about 3 grams of alcohol; and in 82 liters of the urine of a girl affected with diabetes alone, 5 grams of acetone and a very small quantity of alcohol. He believes that acetone and ethyl alcohol are constant constituents of the urine in diabetes, and that they are the product of a peculiar fermentation of glucose, such fermentation being consequent on the formation in the organism of a special acetone-ferment.

J. R.

Chemical Investigation of a Case of Cystinuria. By W. F. LOEBISCH (*Liebig's Annalen*, clxxxii, 231—240).—The author has determined the amounts of urea, uric acid, cystine, and sulphuric acid contained each day during 14 consecutive days in the urine of a young man affected with cystinuria. The urine when first voided was perfectly bright, of yellow colour, without peculiar odour, and always acid, except on one day when vegetable food alone was eaten. On standing for 10 or 12 hours the cystine was deposited in fine loose granules on the sides and bottom of the containing vessel, and presented much the same appearance as calcium oxalate deposited from acid urine. The analytical results showed the presence on the average of 33.28 grams of urea, 0.5545 gram of uric acid, 0.3930 gram of cystine, and 2.439 grams of sulphuric acid in the 1296 c.c. of urine voided daily. The author concludes from these results that the secretion of the nitrogenous decomposition-products of albuminoids is not affected by the formation of cystine.

J. R.

On the relation of Sodium Chloride to certain Animal Fermentation-Processes. By ALEXANDER SCHMIDT (*Pflüger's Archiv. f. Phys.*, xiii, 93—146).—In this paper the author gives the results of his experiments on the coagulation of milk with rennet, the digestion of albumin with pepsin, and describes more fully the influence of neutral salts on the coagulation of fibrin.

1. *The Coagulation of Milk by Rennet.*—By entire removal of the soluble salts the author attained the highest degree of activity of the casein ferment, whence it follows that the alkali-salts contained in the milk and in the gastric juice, especially sodium chloride, influence the coagulation of casein only by hindering its progress.

2. *Digestion of Albuminous Bodies by Pepsin and Hydrochloric Acid.*—The author found, in confirmation of previous experiments, that by the addition of .5 to .6 of sodium chloride to gastric juice containing little or no salt, the fermentative activity is greatly diminished, the time

of solution often increasing in length from 3 to 10 times. Egg albumin boiled in the shell, and therefore containing all the salts, is, he found, much less soluble than that coagulated by dilution with acidulation and boiling, in which case only a part of the soluble and insoluble ash components is retained in the coagulum. For the same reason the latter is dissolved more slowly than albumin coagulated after dialysis. He finds that the transformation into peptone occurs more rapidly in the case of casein than of albumin. The author shows that in the new-born calf less pepsin is formed than in one six weeks old. He thinks, however, that this smaller quantity suffices for its wants.

3. *The Coagulation of Fibrin*.—The author expresses the relation subsisting between the soluble salts and the fibrino-plastic substance in a coagulable fluid as follows:—

1. The proportion of soluble salts remaining constant, the weight of fibrin increases in a diminishing ratio with the proportion of fibrino-plastic substance within certain limits, beyond which it diminishes until coagulation is entirely absent.

2. The proportion of fibrino-plastic substance remaining constant, the weight of fibrin increases in a diminishing ratio with the content of salts within certain limits, beyond which it diminishes until coagulation is prevented.

The first law the author has previously demonstrated; in proof of the latter he describes numerous experiments in this paper. By increasing the amount of fibrino-plastic substance and salts in a coagulable fluid the quantity of fibrin may be increased up to a certain point, this being limited by the quantity of fibrinogenous substance present. The author found that if a coagulable transudation did not coagulate on the addition of fibrin-ferment, it never did so on the further addition of sodium chloride. In those coagulable transudations which coagulated on the addition of fibrin ferment, the addition of from .2 to .5 per cent. of sodium chloride always diminished the amount of fibrin formed. As regards the *rapidity* of coagulation, the author's observations confirm those of Heidenhain with regard to the digestion of albumin by pancreatin. They are to the effect generally that, with an equal proportion of salt, the rapidity increases with the content of ferment up to a certain limit not to be exceeded, and with a constant proportion of ferment it rises with an increase of salt up to a certain point, beyond which it sinks on increasing the salt. With regard to the fibrinogenous substance, the author finds that the amount contained in the pericardial fluid of the horse, and in human hydrocele fluid, is greater than that of the fibrin obtained from the same fluids under the most favourable circumstances. The amount of the product of decomposition is therefore less than that of one of the component albuminous substances. The author concludes that the quantity of fibrin obtainable from a given fluid is variable, and depends on the concurrence of the following conditions:—1. Content of fibrin generators. 2. Content of salt. 3. Content of alkali. 4. Temperature of coagulation. 5. And to a limited degree the content of ferment and hæmoglobin (?).

From experiments described, the author draws the following conclusions:—

1. In a saturated alkaline solution of the fibrin generators, free from salt, and not containing an excess of the dissolving agent, there is formed by the action of fibrin ferment a product insoluble in water and soluble in an excess of alkali, which is not fibrin, but, in presence of neutral alkali-salts in the alkaline solution becomes converted into fibrin. Provided there is no excess of alkali present, almost the whole of the globulin-like substances contained in the fluid become converted into this body.

2. Having shown in previous experiments that in solutions of the fibrin generators in neutral alkali-salts in presence of fibrin-ferment, coagulation occurs (provided there be no excess of the salt), the author thinks that in this case a similar transformation occurs. The same agent which causes the solution of the fibrin generators gives rise also in this case to the conversion of the transformation-product into fibrin.

3. By a sufficiently great excess of alkalis and neutral salts, this transformation of the coagulation substratum is prevented; this substance retains the characters of the globulin-like bodies.

4. The blood contains in its alkalis and salts of alkaline reaction alone, sufficient dissolving agents to dissolve the globulin-like components. The excess, however, of dissolving agents is not so great as to prevent entirely the action of the ferment; a part of the substratum is therefore transformed, the rest remaining in solution as globulin-like body. Ordinarily this residue consists only of fibrino-plastic substance, and can therefore not be converted into fibrin. The *transformed* portion, which is at first retained in solution by the alkaline components of the fluid, is converted by the action of the neutral salts into fibrin.

Experimenting with horse-blood plasma, the author found that saturation with sodium chloride precipitated not only the globulin substances, but also the fermentative product of its transformation.

The fibrin-substances precipitated by sodium chloride from one and the same plasma resemble true fibrin more, the nearer the time at which they are precipitated is to the moment of spontaneous separation of the fibrin. The author applies the term *fibrin* to those only which are insoluble in a solution of sodium chloride, whether more or less soluble in soda. Sodium chloride, he finds, hinders to a certain degree the enclosure of fibrin-ferment by fibrino-plastic substance. With regard to the action of alkalis on the intermediate product of coagulation, the author finds that this consists in a further transformation of the same into a slimy mass, having the same characters as that obtained by Semmer and the author from the stroma and nuclei of amphibian blood-corpuscles by means of dilute soda.

In conclusion the author likens the coagulation of fibrin to an inverted digestion.

E. C. B.

The Albuminous Ferment of the Pancreas. By S. PODOLINSKI (*Pflüger's Archiv. f. Physiologie*, xiii, 422—443).—Heidenhain found that the albumin-dissolving ferment of the pancreas does not exist in the living gland, but appears first in the secretion. It can,

however, form itself in the tissue of the gland after death, and this conversion takes place (a) on exposing the organ to the atmosphere; (b) on diluting the glycerin extract of the fresh gland with water; (c) on treating the substance of the gland with acids.

This paper describes a series of experiments made with the view of accurately discovering the cause of this *post-mortem* formation of pancreatin. And the experiments show this conversion to be, in all three instances, due to the action of oxygen on the substance contained in the living gland, viz., zymogen.* F. J. L.

Chemistry of Vegetable Physiology and Agriculture.

Modification of Starch in Vegetables. By M. MERCADANTE (*Gazzetta chimica italiana*, vi, 97—98).—The author does not agree with Frank that the starch in the cells of the medulla and the medullary rays is transformed into gum without any change of aspect or form, for he finds that the gum first appears in the cells contemporaneously with the starch, the latter occupying the centre of the cellular mass, whilst the gum forms concentric layers outside it. In the spring, the starch gradually dissolves, whilst the gum increases, and now forms a deposit in the interior of the cells; with the progress of the vegetation, the starch disappears, serving as food for the young growth, and leaving the cells empty. That this starch is converted into soluble starch is shown by the cold aqueous extract of the medulla giving a precipitate with baryta-water. C. E. G.

Formation of Sulphuric Acid in Seedlings. By E. SCHULZE (*Landw. Versuchs-Stat.*, xix, 172—176).—Plants are known to possess the power of utilising the sulphur of sulphates for the production of sulphy-organic compounds, a process by which the sulphate undoubtedly undergoes reduction. It was, however, discovered during some researches conducted by the author, in conjunction with Umlauf and Urich, that, during the growth of lupine seedlings in the dark, exactly the contrary takes place, viz., that the amount of sulphuric acid increases at the expense of sulphur pre-existing in organic combinations in the seed. Subsequent experiments confirm this, and show that the increase in sulphur is most probably due to the decomposition of sulpho-albuminoid compounds. H. H. B. S.

The Germination of Lupine Seeds. By E. SCHULZE, W. UMLAUF, and A. URICH (*Deut. Chem. Ges. Ber.*, ix, 1314).—Non-germinated seeds of lupines contain 45 per cent. of conglutin and albumin, but after germinating for 15 days in the dark, only 8 per cent. of albuminoids remain, and 60 per cent. of their nitrogen is found as

* This paper was written before the appearance of Kühne's research upon the albumin-dissolving ferment of the pancreas, termed by him *Trypsin*. (*Verhandl. d. Heidelberg. naturhist. Ges.* 5, i.)

asparagine; other amides and ammonia are also formed, but only in small quantity, while the sulphur is converted into sulphates.

C. S.

Absence of Leucin in the Products of Germination of the Graminaceæ. By M. MERCADANTE (*Gazzetta chimica italiana*, vi, 100—101).—The germinated seeds of *Triticum sativum*, *Hordeum vulgare*, *Avena sativa* and *Zea Maïs*, were each boiled with water and the clear liquid filtered and concentrated. On testing the solution for leucin by nitrate of mercury, no precipitate was obtained, neither did the liquor give any coloration with sodium hypochlorite in presence of phenol, as it would have done had leucin been present. This result affords further evidence of the difference between the nitrogenous principles of the Graminaceæ and those contained in the Leguminosæ.

C. E. G.

Gases in the Fruit of the Bladder Senna. By C. SAINT-PIERRE and L. MAGNIEN (*Compt. rend.*, lxxxiii, 490).—The gas in the fruit of *Colutea arborescens* is not common air, but a mixture poorer in oxygen, and containing 0·50 to 2·32 per cent. of carbonic acid. The authors have found that in these fruits, although their colour is green, oxygen gas is absorbed and carbonic acid gas given out, by night as well as by day; and that the amount of carbonic acid produced is greater than the oxygen absorbed would furnish. In this plant there are, therefore, green organs, which act like the animal tissues and the coloured parts of other vegetables.

R. R.

Composition and Nutritive and Manurial Value of Kapok-cake. By G. REINDERS (*Landw. Versuchs-Stat.*, xix, 161—164).—The kapok-tree (*Eriodendron anfructuosum*) of Java and the Indian Archipelago, bears a seed resembling, in many respects, that of the cotton-plant. Like cotton-seed, it is covered with a wool, which, though less suited for spinning, yet has long been used in India and the Netherlands for filling bolsters, &c.

The following analyses show the composition of a trial-cake made from this seed, as compared with that made from seed of the cotton-plant:—

	Kapok cake.	Cotton cake.
Water.....	13·28	12·60
Nitrogenous (albuminous) compounds ..	26·34	20·62
Fat.....	5·82	6·36
Non-nitrogenous extractive matter	19·92	35·42
Woody fibre	28·12	20·36
Ash.....	6·52	5·64

It is probable that kapok-seed may be employed in the Netherlands for adulterating linseed-cake, although it is not mentioned by Voelcker (*Jour. Roy. Agricultural Soc.*, vol. ix, Part I) among the seeds discovered by him to have been used for this purpose. The ash of the seed contains 28·5 per cent. phosphoric acid and 24·6 per cent. potassa; it would, consequently, have about the same manurial value as linseed or rape.

H. H. B. S.

Action of Sea-water upon Land. By G. REINDERS (*Land. Versuchs-Stat.*, xix, 190—214).—Land that has been submerged by sea-water generally proves sterile for some time, and indeed, in some cases, has remained so for 10 or even 20 years. This sterility can be traced to the co-operation of the three following chemical causes, in addition to the injury produced mechanically by the inundation:—
 *1st, to the introduction of too great a proportion of chlorine salts; 2nd, to the hygroscopic property communicated to it, preventing it from properly drying; and 3rd, to the formation of ferrous sulphate, which is known to exert a very prejudicial effect upon plant-growth. This salt is produced in the soil thus: the calcium and magnesium sulphates becoming reduced to sulphides by the organic matter, react upon the iron compounds forming iron sulphide, which is then oxidised to sulphate by exposure to the air.

Land which has been thus damaged should be drained as quickly as possible and sown with grass or clover, and allowed to rest. Experience shows that it recovers its fertility sooner, if treated in this way than if cultivated all the year round as arable land.

H. H. B. S.

Notes on the Fermentation of Fruits plunged into Carbonic Anhydride. By J. JOUBERT and CH. CHAMBERLAND (*Compt. rend.*, lxxxiii, 354).—A number of fruits (cherries, plums, gooseberries, &c.), chosen as perfect as possible, were placed in tubes partially filled with carbonic anhydride, over mercury—one fruit only in each tube. When the volume of gas ceased to augment, the fruits were withdrawn and the interior pulp extracted, every precaution being taken to prevent its contact with the outer skin. The microscopic examination of the pulp never showed the presence of ferments. Certain round granulations were seen, but they may be found in fruits which have not been plunged into carbonic anhydride; moreover, the pulp extracted in the manner mentioned does not cause the fermentation of grape must into which it is introduced. This difference of results from those obtained by Fremy is considered to be due to the lengthened washing to which he subjected his specimens, and to their being piled together in a flask.

C. H. P.

Cellulosic Fermentation produced by Vegetable Organs; and probable Utilisation of Sugar for the production of Cellulose in Vegetation. By E. DURIN (*Compt. rend.*, lxxxiii, 355).—It is shown that plants contain some substance capable of exciting cellulosic fermentation, from which it appears that the sugar assists in the production of cellulose in vegetation.

C. H. P.

The Microzymes of Germinated Barley and of Sweet Almonds, as producers of Diastase and Synaptase, in reference to a Note of Pasteur and Joubert. By A. BÉCHAMP (*Compt. rend.*, lxxxiii, 358).—The microzymes of the pancreas of barley, natural or germinated, of almonds and of yeast, possess the same chemical functions as pancreazymose, diastase, synaptase, and the zymase of beer-yeast.

C. H. P.

On Pure Yeast. By MORITZ TRAUBE (*Deut. Chem. Ges. Ber.*, (ix, 1239—1245).—When ordinary beer-yeast is added to a filtered decoction of yeast to which sugar-candy and alcohol have been added, the products of the action thereby set up vary with the proportions of the ingredients, more especially with the proportion of alcohol. A decoction of 40 grams of yeast in 200 c.c. of water, made up to 1 liter with water holding in solution 100 grams of sugar-candy (Pasteur's liquid), undergoes alcoholic fermentation almost completely on addition of a small quantity of yeast. But if the proportion of sugar be reduced to one-half, the formation of yeast-cells goes on with difficulty, whilst bacteria develop rapidly, and in a few days the liquid becomes putrid. The effect of alcohol added to the fermentable liquid is very striking. From numerous experiments with varying proportions of this liquid, the author arrives at the following conclusions:—

1. The development of bacteria and of all other disease-ferments, as well as of *Mycoderma vini*, is considerably retarded by a small quantity of alcohol (2·8 per cent.), and is entirely prevented by a larger quantity (5·6 per cent.).

2. The development of yeast is also retarded by alcohol, but it still goes on in solutions containing 8·2 per cent.

3. Hence, *pure yeast* is developed in appropriate solutions containing from 5·6 to 8·2 per cent. of alcohol.* It appears to be unnecessary to boil the liquid to be fermented before adding yeast, provided it contains the necessary proportion of alcohol.

It is evident that when once a small quantity of pure yeast has been obtained as above, it may be used to obtain a larger quantity by introducing it into a previously boiled fermentable solution free from alcohol. Pure yeast may thus be developed even in solutions rich in albuminous matters, and the fact that it can be so developed is the best possible proof of the purity of the yeast added. J. R.

Analytical Chemistry.

The Iodine and Starch Reaction. By E. PUCHOT (*Compt. rend.*, lxxxiii, 225—226).—The sensitiveness of the iodine and starch reaction is greatly impaired by the presence of certain organic nitrogenous bodies. Thus, albumin introduced into the water which holds in suspension iodide of starch, causes the disappearance of the colour; and if albumin be mixed with a solution of starch, the addition of a saturated aqueous solution of iodine produces no coloration, unless the iodine be added in great excess. As albumin added to an aqueous solution of iodine causes the colour to vanish, there probably is, in the above-described cases, a direct combination between the iodine

* This is true only at temperatures not exceeding 15°. Subsequent experiments at 25° showed that the yeast developed in solutions containing as much as 10·6 per cent. of alcohol is not quite pure.

and the albumin. If a little albumin be mixed up with starch in a mortar, and iodine, drop by drop, be allowed to fall upon the mixture, each drop produces a temporary blue stain, which disappears as the liquid, by spreading, meets with a sufficient quantity of albumin.

R. R.

Detection of Traces of Phosphoric Acid in Toxicological Researches. By F. SELMI (*Gazzetta chimica italiana*, vi, 34—35).—The method consists in bending the extremity of a platinum wire into a ring, dipping it into the liquid suspected to contain phosphoric acid, and then inserting it into the centre of a hydrogen flame at a point somewhat nearer to the orifice than to the apex of the flame. The minutest trace of phosphoric acid immediately communicates a green tinge to the flame. In using this test, sodium must be absent,* and the phosphoric acid in the free state.

C. E. G.

Dittmar's Method of Determining the amount of Chromium in Chrome Ores. (*Dingl. polyt. J.*, cxxi, 450).—This method is based on the knowledge of the fact that powdered chromium ores are readily dissolved in a flux consisting of 2 parts of borax fused together with 3 parts of alkaline carbonates. The mixture formed absorbs oxygen during the fusion, and also while in contact with the air, and this results in a conversion of the oxide of chromium to a chromate. 0.5 gram of the ore is fused with 5—6 grams of the above-mentioned flux in a covered crucible for about five minutes. The lid of the crucible is then removed, and the mass heated very strongly with constant stirring, until the whole of the ore has been dissolved, when the fusion is still continued for about three-quarters of an hour. The fused mass is digested with water, heated over a water-bath with the addition of a few drops of alcohol, so as to reduce any manganates if present; the liquid is filtered, and the residue washed with hot water. The filtrate contains the whole of the chromium present in the ore in the form of a chromate, which is determined, according to Penny's method, by dissolving a certain quantity of iron wire in hot dilute sulphuric acid, cooling the solution very quickly and adding the chromate. The mixture is then titrated back with potassium bichromate.

Experiments have shown that one fusion suffices to dissolve the whole of the chromium present in the ore; the utmost difference when two fusions were made was not more than 0.3 per cent. of oxide. Although the platinum crucibles employed showed no signs of alteration, the residue, after fusion, gave a notable quantity of a platinum salt when dissolved in dilute sulphuric acid. It is, therefore, not advisable to simplify the above method by dissolving the whole fused mass in dilute acid and then titrating the solution.

D. B.

A new Chemical Test for Alcohol. By EDMUND W. DAVY (*Proceedings of the Royal Irish Academy* [2], ii, 579—582).—A solution of 1 part of molybdic acid in 10 parts of strong pure sulphuric acid

* The difficulty occasioned by the presence of sodium may be overcome by examining the flame with the spectroscope.—Note by Abstractor.

is warmed gently in a porcelain capsule, and a few drops of the liquid to be tested are allowed to fall gently into the capsule. If alcohol be present, a blue coloration becomes apparent, either immediately, or after a few moments. This coloration disappears after exposure to the air, but only in consequence of absorption of moisture, for on evaporation the colour again appears. This colour is also produced by methyl, propyl, butyl, and amyl alcohols, ether, and aldehyde. The test is especially useful for detecting alcohol in chloroform or in chloral hydrate. Its sensitiveness is so great that alcohol may be detected in one drop of a mixture of 1 part of alcohol with 1,000 of water.

W. R.

Rhodeine, a New Test for Aniline. By E. JACQUEMIN (*Comp. rend.*, lxxxiii, 226—229).—The sensitiveness of the well-known reaction of aniline with hypochlorites is such that one part in 10,000 may be detected. With a greater dilution hypochlorites give only a very slight brown tint, if they produce any visible effect at all. But the author has found that the further addition to the brown or colourless solution of a few drops of a very dilute solution of ammonium sulphide (one drop in 30 cc. of water) develops a magnificent rose colour, by which so small a proportion as one part of aniline in 250,000 may be recognised. This new colour, which is very fugitive, and disappears immediately if an excess of sulphide be added, the author proposes to designate as *rhodeine*. He did not obtain similar results with oxidising or reducing reagents other than those above-named, nor did toluidine, &c., produce any such effects.

R. R.

Phyllocyanin as a Reagent. By G. PELLAGRI (*Gazetta chimica italiana*, vi, 35—38).—The blue colouring matter of flowers, phyllocyanin, is extremely sensitive to minute traces of free alkali, and although the blue solution cannot be preserved, yet when a small quantity of sulphuric acid is added, the red solution thus produced may be kept for a long time without undergoing alteration. The quantity of acid added should not be so large as to give a distinct red colour, but merely enough to change it to a dark purple intermediate between the blue and red. In this state it is capable of showing distinctly the alkaline reaction caused by the presence of ammonia in rain-water, or by the plumbic hydrate in water which has been in contact with metallic lead. Added to a solution of one part of potassium hydrate in 1,200,000 parts of water, it produces a permanent blue colour, whilst with a solution in 200,000 parts of water a permanent green is obtained. It is, therefore, a much more delicate test than litmus, which scarcely gives any reaction with the last-mentioned solution.

Paper prepared with a solution of phyllocyanin must be kept in well-closed vessels; for although unaffected in a vacuum, or by air which has been exposed over sulphuric acid, yet when it is exposed freely to the air, the ammonia present in it turns the colour blue.

The phyllocyanin is best obtained from the iris, the violet, or the purple verbena, by treating the petals with a small quantity of warm

water; sulphuric acid is then added until it assumes a purple colour, and the solution is preserved in a closed vessel excluded from the light.

C. E. G.

Determination of Theine in Tea. By B. W. MARKOWNIKOFF (*Deut. Chem. Ges. Ber.* ix, 1312—1313).—15 grams of powdered tea, 15 grams of *magnesia usta*, and 500 cc. water are boiled and filtered; the residue washed with hot water; and the filtrate, after addition of magnesia and sand, evaporated to dryness. The residue is exhausted with hot benzene, which is then evaporated and the residue weighed. Young leaves contain more theine and less ash than old ones. The author believes that the quality of tea does not depend on the quantity of theine, but on that of tannic acid, essential oils, &c.

C. S.

Modification of the Process for Extracting the Poisonous Alkaloids from the Viscera. By F. SELMI (*Gazzetta chimica italiana*, vi, 32—34).—As it has been found that the acidulated alcoholic extract containing the alkaloids frequently undergoes alteration when evaporated in the ordinary way, the author concentrates the solution in small portions at a time at about 65° in a porcelain dish, accelerating the evaporation by means of a fan. The aqueous liquid thus obtained is filtered, concentrated, and agitated with ether, after the addition of baryta. If the ethereal solution is coloured it must be evaporated, mixed with basic acetate of lead, exposed to the air for 24 hours, and then filtered from the carbonate of lead and the coloured lead lake. The excess of lead is then removed by sulphuretted hydrogen, the solution evaporated, and the alkaloids again taken up by ether after the addition of baryta; even then the ethereal solution may contain foreign matters which modify the reactions or impede crystallisation. If, however, an ethereal solution of tartaric acid be added, a white precipitate is formed, which usually contains the whole of the alkaloid as tartrate. In some cases the alkaloids may be precipitated as carbonates by passing a current of dried carbonic anhydride into the ethereal solution; if not, on adding about one-third or one-fourth of the volume of distilled water and continuing the passage of the gas, the carbonates of the alkaloids are dissolved by the water, whilst the foreign matters remain in the ethereal solution. Amylic alcohol extracts may with advantage be treated in a similar manner.

The coloured precipitate above mentioned should also be carefully examined, suspending it in water and decomposing it by sulphuretted hydrogen.

In the case of volatile alkaloids the author separates them by distilling them off in the vapour of absolute alcohol, and condensing the vapours in a receiver containing an alcoholic solution of tartaric acid.

C. E. G.

Technical Chemistry.

Chemical Examination of Twelve Colours found at Pompei. By P. PALMERI (*Gazzetta chimica italiana*, vi, 39—45).—Of these colours three were yellow, one consisting of a yellow ferruginous earth mixed with white clay to make it paler; another a limonite (hydrocarbonate of iron) mixed with gypsum; the third a yellow ochre, mixed with calcium carbonate. Of the two greens, one, a bright green, was found to contain ferrous and ferric oxides, alumina, lime, silica, and carbonic anhydride. It is apparently identical with "*terra verde*," which Pliny mentions (xxxv, 29). "*Sunt etiamnum novitii duo colores et vilissimi; viride quod Appianum vocatur. . . . Fit et ex creta viridi.*" The other green contained copper, but, from its state of aggregation, the author thinks it must have become considerably altered in the lapse of time. Five red and red-brown colours were found to be ochres; one probably "*minio falso*," the "*minium secundarium*" of Pliny; another sample was a mixture of fragments of various descriptions, and the twelfth, which was of a rose colour, was found to consist of a white clay, mixed with a little chalk and phosphate, and coloured with a rose colour of organic nature. It forms a purple lake with alumina, and its reactions, when compared with those of cochineal and madder lakes, exhibit a marked discrepancy in several instances, especially under the action of chlorine and bromine, the Pompeian colour being exceedingly stable. The author is of opinion, judging from various statements in Pliny, the text of which he quotes, that it is not improbable that this extremely solid and fast rose-colour employed by the Pompeians may have been obtained by saturating a white clay with the compound colour produced from Tyrian purple (from *Purpura* or *Murex*), extract of Kermes (*Coccus Ilidis*, from *Quercus coccifera*), and madder extract. This point he hopes to determine experimentally. C. E. G.

Temperature and Composition of Gases evolved from Ultramarine Furnaces. By F. FISCHER (*Dingl. polyt. J.*, ccxxi, 468—473).—The temperature of the ovens was ascertained with a Siemen's electric pyrometer (*Dingl. J.*, 1875, 217, 291), and the composition of the gases escaping determined by Orsat's apparatus, which has been recently improved by Aron. The fact that the absorption and the measurement of the gases take place in two distinct tubes, by which the determination of the separate constituents in the gas after it has been measured is greatly facilitated, renders this apparatus more suitable for analysis than the use of Winkler's burette. The sulphurous acid was determined with $\frac{1}{10}$ normal iodine solution. The acids absorbable by potash were determined by Orsat's apparatus using oil as the indicator, so as to prevent the solution of sulphurous acid in water. The difference of the two determinations is calculated as carbonic acid, but since the gases are always coloured more or less white from the presence of sulphuric anhydride, which is also absorbed by potash lye, the percentage of carbonic acid will be somewhat high.

The following table gives the results of analyses made with a crucible furnace:—

Crucible Furnaces lighted at 6 a.m.

No. of Experiment.	Time.	SO ₂ .	CO ₂ .	CO.	O.	N.	Temperature.	Remarks.
	14th July. hour. min.							
1	9 0	2·67	9·93	0	6·4	81·0	—	{ Fire burnt down. White vapours.
2	9 30	2·58	10·12	0	7·1	80·2	473	{ Ditto.
3	10 30	3·28	12·12	0	4·8	79·8	522	{ Ditto. Dampers partly closed.
4	11 0	2·89	10·01	0	6·2	80·9	696	{ Ditto.
5	11 30	3·04	8·26	0	8·7	80·0	—	{ Ditto.
6	12 0	2·76	10·54	0	6·2	80·5	—	{ Ditto.
7	12 40	2·10	10·80	0	6·0	81·1	700	{ Ditto.
8	2 50	2·27	12·63	0	3·0	82·1	—	{ Air shut off by layers of bricks.
9	3 40	3·12	17·88	0	0	79·0	—	{ Immediately after stoking. Vapours not white.
10	3 47	2·95	13·05	0	2·1	81·9	733	{ Upper layer of bricks removed, thus allowing more air to pass through.
11	4 0	3·25	—	0·1	0·4	81·1	—	{ Immediately after stoking. Slight separation of soot.
12	4 20	1·48	—	0	10·4	82·5	—	{ Not stoked; there- fore burnt com- pletely. Vapours white, not trans- parent.
13	4 40	1·40	—	0	4·8	82·6	714	{ About 10 minutes after stoking.
14	5 10	0·70	—	0	13·8	81·7	—	{ Completely burnt. Vapours white.
15	5 45	0·34	—	0	16·3	80·8	668	{ Ditto. Air shut off.
16	6 10	0·47	—	0	11·1	82·5	—	{ Ditto.
17	6 16	1·11	—	0	3·4	81·1	—	{ Immediately after stoking.
18	6 30	0·64	—	0	10·1	83·1	730	{ Not stoked; burnt completely.
19	15th July. p.m. 5 0	0·01	—	0	17·9	80·4	627	{ Not stoked for 9 hours; all open- ings shut off by clay.

It seems that the temperature of the furnaces during the ultramarine process is about 700°. The gas analyses show that the process is more quickly conducted in crucible furnaces than in muffle furnaces. It is next to impossible to use the gas mixture profitably for the lead-

chamber process, as the gases are very much diluted and are not evolved regularly. The reason why a crucible furnace requires 50 kilos., and a muffle furnace 146 kilos. of best Westphalian coal for every 100 kilos. of blue charge is sufficiently explained by the fact, that through the latter form of furnace a larger quantity of air is always passed. Carbonic oxide is mostly absent in these gases. D. B.

Hardening of Steel. By A. JAROLIMEK (*Dingl. polyt. J.*, ccxxi, 436—446).—It is stated that boiling water does not form the only cooling liquid which hardens steel, but that under circumstances water at a temperature of 150° or more will do so, and that boiling hot oil, fluid lead, fluid tin, and even fluid zinc—a cooling liquid of about 400° of heat—will also give similar results. This latter fact is worthy of notice, as it has in general been assumed that steel cannot be hardened unless it be brought down very quickly to a much lower temperature, and that hardened steel softens considerably when exposed to a temperature of 300°; but experiments have shown that the hardness of steel depends upon the quickness with which it is reduced from a temperature of about 500° to one somewhat under 500°. Although the above-mentioned metals are able to harden steel, it was nevertheless found that their hardening property could not at all be compared with that of water, this property being in fact influenced not merely by the temperature and the conductivity of the cooling substance, but also by its capacity for heat, its boiling point, and, in the case of a low boiling point, by the amount of latent heat which the vapour contains. For instance, alcohol vaporises very readily, and as it contains but little latent heat, hardens steel but very badly. Now it is well known that a metal which is heated to a temperature of 1000° or even only to 500° must be surrounded by a temperature which renders the existence of water of an ordinary pressure quite impossible. So long as hardened steel possesses this temperature—which it in fact retains until its hardening commences—it cannot be in immediate contact with water, and when plunged into that liquid, must be surrounded by a layer of vapour, which is apt to hold back portions of water near the steel and thus prevent a regular hardening of the latter. It is, of course, improbable that under these circumstances the steel would give up its heat to the water by direct conduction, and as the layer of steam between the metal and the water cannot be superheated to any material extent at so slight a pressure, we must suppose that the water becomes heated by radiation, the layer of water separated by the steel evolving a constant stream of vapour, which condenses on the upper portions of the layer of water. It is shown by calculation that one kilo. of steel requires about 0·2 kilo. of water at 20° to lower its temperature from 1000° to 300°; but the reason why a much larger quantity of water is actually required is sufficiently explained, if we consider, that (1) the steel has to be moved about in the water; otherwise the formation of vapours would prevent its hardening. (Relying on this fact, it was possible to harden steel under hot water, alcohol, or turpentine.) (2.) The vapours condense in the water, and heat a small quantity of it too strongly. Thus it seems that it would be possible to harden steel with a small

quantity of water, could the vapour escape as quickly as it is formed. Such, however, is not the case, and the above condensation can, therefore, be facilitated only by the following operations:—(1.) By plunging the hot steel slowly into the water, the surface of the latter is chiefly acted upon, the vapours having easy access of escape in the air. This method is applicable in cases where the metal above the water remains sufficiently hot to be hardened, e.g., files and other similar articles are easily hardened by this process. (2.) A hot and powerful stream of water escaping from a steam-boiler, or an ordinary stream of water, facilitates the hardening by carrying off the vapours as quickly as they are formed. (3.) The most satisfactory method is that by which the steel is hardened by means of a thin spray. In this condition the water is largely mixed with air, which, having a very quick and strong action, not only occasions a quick vaporisation, but also carries off the vapour formed in a much more complete way than any of the above-mentioned agents. In practice the degree of hardness of steel depends upon the annealing of the latter—a process which always follows the hardening operations. In order to obtain a medium hardness, the steel is cooled slowly throughout the whole of the operation, or it is cooled very quickly to 400° , and afterwards slowly. The former method did not answer in practice, a quick cooling being almost indispensable if satisfactory results are to be obtained. The resulting steel was either of a very hard or of a very soft nature. With regard to the annealing methods, similar experiments were undertaken, the results of which seemed to show that the most profitable form of applying the cooling liquid was when a spray of water was blown on to the steel.

In conclusion, it is stated that fused metals, especially tin, answer very well for hardening small articles. The author was able to harden a steel wire, 3 mm. thick, in a tin bath of 400° of heat, the wire again becoming soft, when it was left in a bath of 350° . On account of the smaller heat-capacity of tin, a large quantity of it is required. One part of steel requires about 45 parts of tin to cool it from 1000° to 300° , if the temperature of the bath before use is 250° , and has not to be raised over 300° . In another paper a description of the fusion of the steel before it is hardened, and further results with regard to the above operations will be given. D. B.

Burnishing of Iron. By P. HESS (*Dingl. polyt. J.*, ccxxi, 94—95).—The surface of the iron is painted over with linseed oil and heated, whereby, together with separated carbon, ferroso-ferric oxide appears to be produced, which forms the essential protecting layer. Articles which cannot be heated may be dipped into an acidulated solution of ferric chloride, whereby a black layer of ferroso-ferric oxide is formed, which when dipped into hot water, becomes firmly fixed on the iron, so that after drying it can be rubbed with linseed oil. The formation of this layer takes place by the reducing action of the iron on the oxide and its salts: $4\text{Fe}_2\text{O}_3 + \text{Fe} = 3\text{Fe}_3\text{O}_4$.

The advantages of burnishing with ferroso-ferric oxide (magnetic iron ore or smithy scale burnishing) consists in the fact that it is done much more quickly than the burnishing with ferric oxide, and that it

is more beneficial to the iron than the latter. By using cuprous sulphide a fine bluish-black layer is obtained, which forms a good protection against rusting. The iron has only to be placed in a solution of cupric sulphate for a few minutes, until a fine copper coating is formed on its surface, which after having been washed with water, is treated with a solution of sodium hyposulphite (thiosulphate) slightly acidulated with hydrochloric acid, when a bluish-black coating of cuprous sulphide is obtained, which is unaffected by air and water. The surface is then washed with water, dried, and polished. D. B.

The Uses of Patent Colours. By R. GLANZMANN (*Dingl. polyt. J.*, ccxxi, 473—477).—On account of their simple application, their perfect coloration, and their cheapness, the patent colours described by Croissant and Bretonnière are now largely used in the dyeing of yarns. These organic colours, containing large quantities of sulphur, are manufactured by various firms and under different names. The author described (*Bull. de Rouen*, 1876, 61) a preparation which was brought into commerce by Poirrier, under the name of "Cachou de Laval." It seems to be prepared from sawdust, and is in the form of large blackish-blue very porous lumps, which are very hygroscopic, smell strongly of sulphuretted hydrogen, and contain $1\frac{1}{2}$ to 2 per cent. of water. It is very readily soluble in water, its aqueous solution having a strongly alkaline reaction, and being precipitated by acids, with evolution of sulphuretted hydrogen, elimination of sulphur, and formation of a darkish brown precipitate difficultly soluble in alkalis. In spite of the valuable property which this colouring matter shares with the other patent colours, of being fixable on cotton without the use of a mordant, or even without steam, and in spite of their resistance to the action of light, acids, and soaps, the author has nevertheless come to the conclusion that this category of colours will not find much application to the printing on cotton. These colours are easily acted upon by chlorine, and do not form shades which are much valued for cotton prints. Glanzmann has made several dye experiments with Poirrier's "Cachou de Laval," and has obtained very good results from the "dark cachou" which he produced in a bath of 50 grams of colouring matter fixed by a solution of 5 grams of potassium bichromate in 1 liter. A bath containing 3 grams of colouring matter in 1 liter yields, after treatment with potassium chromate, a light grey colour with a yellow tinge. By dissolving 10 grams of the cachou in water, mixing the solution with 20 grams of real cachou (dissolved in 10 c.c. of soda-lye of 1.208 sp. gr. and 500 c.c. of water) and making the total up to 1000 c.c., yarn acquires a fine dark bronze colour when it is left in this bath at 75° for a quarter of an hour, and afterwards fixed with the chromate, or, still better, with a nitric acid bath of 2° B. The various shades resulting from the colouring bath are greatly influenced by the fixation bath. Potassium bichromate gives the darkest shade of colour; nitric acid and nitrate of iron with lead acetate give a grey colour having a slight yellow tinge; ferrous sulphate (5 grams in 1 liter) with sulphuric acid of 1.004 sp. gr., or, better, copper vitriol (5 grams in 1 liter), give a grey with a blue tinge. This shade forms the main use

of the patent colours, serving as a ground colour for indigo blue, by which a considerable saving of valuable colouring matter is occasioned, whereas the stability of the blue is not in the least injured. In Germany this colour is sold in the form of a liquid under the name of "Indigoersatz" (indigo substitute). In the *Deutsche Industrie-Zeitung*, 1876, 43, a description of a second use of this shade as a finishing colour for chemical blues is given. Yarns, either white or steeped, are passed through a solution of nitrate of iron rendered blue by yellow prussiate of potash, and finished with indigo substitute. The yarn patterns dyed in this manner obtain either a deep black or a very fine bluish-black colour. The former colour is obtained by leaving 25 kilos. of boiled yarn in a bath of sumach (5 kilos.) for 12 hours, and then in a bath of nitrate and lignate of iron (2 kilos. of nitrate of 1.525 sp. gr., and 3 kilos. of lignate of 1.133 sp. gr.) for half an hour. The yarn is brought into a chrome bath (350 grams of red potassium chromate), and lastly dyed in a hot bath of indigo substitute (2.5 kilos.) to which 250 grams of quercitron extract has been added. After washing with soap, the yarn is washed with water and dried. The bluish-black shade is obtained by allowing the same quantity of yarn to remain in a bath of 5 kilos. of sumach for 12 hours, then in a bath containing 5 kilos. of nitrate of iron. It is brought into a bath of 1.5 kilo. of yellow potassium prussiate, to which 0.5 kilo. of hydrochloric acid are added, and having passed it through this bath, 2.5 kilos. of nitrate of iron are added to the latter, and the yarn treated therewith. Its further treatment in the chrome bath and the indigo-substitute baths (3 kilos.) is analogous to that of the black dye.

D. B.

The Present State of the Sugar Industry in France, and a few Experiments on the Use of Lime in the Clarifying Process. By A. LAMY (*Dingl. polyt. J.*, ccxxi, 64—68).—After pointing out that the manufacture of sugar in France has of late years become less profitable than formerly, in consequence of the great excess of production over home consumption, and the keen competition in foreign markets, the author proceeds to indicate the methods which appear to him best adapted to remedy the evil. These are:—1. The endeavour on the part of the cultivator to produce roots containing a large percentage of sugar rather than roots of great size. 2. Increased attention to the methods of extracting and purifying the juice.

The French beetroot contains only from 5 to 6 per cent. of its weight of sugar, whereas from German and Austrian roots 7 to 8 per cent. are obtained; but experience has shown that with proper care a root of the same richness in sugar can be produced in France. Manufacturers have until recently bought the root according to its weight alone, without taking into consideration the percentage of sugar, and to increase their crop many farmers have employed seeds or chemical manures which were favourable to the formation of large roots. In Germany, however, the mode of levying the duty does not induce farmers to obtain a large bulk of material, but to obtain a large percentage of sugar in comparatively a small quantity of roots. The second and third conditions, which require improvement in that country, are the

extraction and the chemical purification of the sap. In a recent paper M. Pésier discussed the excessive use of lime in the clarifying process. The considerable increase in the weight of the scum, which contains about 50 per cent. of the sap, occasions a loss amounting to 200 kilos. for every 100,000 kilos. of roots. To justify the use of this excess of lime, it is usual to allege the fineness of the white sugar of first crystallisation thereby obtained, the quick and complete decolorisation of the sap, and the necessity of fixing with the lime the total quantity of sugar in the form of a saccharate. But although the existence of a lime saccharate at a temperature of 35° has been generally assumed, it has never been proved. Pésier has made a large number of alkalimetric determinations, the results of which seemed to show that at a temperature of 35° a saccharate does not exist, still less, therefore, at 60° or 70° , at which temperature the addition of the lime takes place. With the view of clearing up these contradictions, Lamy undertook the following experiments. In the first place the quantity of lime was determined which would dissolve 100 parts of a 10 per cent. sugar-solution at 30° , 50° , 60° , 70° , and 100° , if 1 to 2 per cent. of lime were added, a proportion generally taken in practice. The slaked lime and the sugar-solution were mixed at the trial temperature and left in contact for three hours, with frequent shaking. The same quantities of lime were added at 50° , 60° , and 70° , the temperature allowed to rise gradually to 100° , and the liquid filtered very quickly at this temperature. The lime in solution was then titrated. The results are shown in the following table:—

Solubility of Lime in a 10 p. c. Sugar Solution, using 2 grams of Lime for 100 parts of the Solution.

Temperature.	Lime dissolved in 10,000 grams of the sugar solution.	Lime deposited in 10,000 grams of pure water.	Difference showing the lime combined with the sugar.	Lime necessary for a monobasic saccharate.	Excess of lime necessary for the formation of a saccharate, over that combined with the sugar.
	grams.	grams.	grams.	grams.	grams.
100	15.5	6.0	9.5	149	+ 139.5
70	23.0	7.9	15.1	"	+ 133.9
50	53.0	9.6	43.4	"	+ 105.6
30	120.0	11.7	118.3	"	+ 80.7
15*	215.0	13.0	202.2	"	- 53.0
0	250.0	14.0	236.0	"	- 87.0
50—100	18.5	6.0	12.5	"	+ 136.5
60—100	17.0	6.0	11.0	"	+ 138.0
70—100	16.0	6.0	10.0	"	+ 139.0

* The numbers corresponding with the temperatures 15° and 0° , were obtained by saturating the sugar-solutions with an excess of lime.

The conclusions to be drawn herefrom are:—

(1.) The quantity of lime dissolved in the sugar-solution increases in the same ratio as the temperature decreases. The same applies to the solution of lime in pure water.

(2.) By deducting the quantities of lime dissolved in sugar-water (col. 2) from those dissolved by pure water (col. 3) at the same temperature, numbers are obtained which correspond with the absorption of the lime by the sugar alone. It is strange, however, that these numbers vary with the temperature, and are much higher than those corresponding with the solution of lime in pure water.

(3.) By comparing the numbers in column 4 with 149 of column 5—a number which gives the quantity of lime to be dissolved so as to form a monobasic saccharate—we find that they are lower than this, and so much the more the higher the temperature is than 30°. The slight differences of the numbers in column 6, which correspond with the temperatures 100°, 50—100°, 70—100°, are sufficiently explained by the difference of time during which the solutions were kept at 100°, and by the difficulty of obtaining a saturation at this temperature.

(4.) The quantity of lime absorbed by the 10 per cent. sugar solution may rise with the fall of the temperature so much that at 0°, for example, it surpasses the quantity necessary for the formation of a monobasic saccharate more than 50 per cent. With regard to pure sugar-solutions, therefore, the quantity of fixed lime is larger than that which pure water dissolves at the same temperature, and even at 100°; but it is much lower than that necessary for forming a monobasic saccharate at 30—70°.

In conclusion, Lamy gives a description of Marot's new method, which is based on the idea that it is not the true mineral salts which hinder the manufacture of sugar, but rather the salts with mineral bases which are combined with organic acids and neutral bodies. The organic substances left in the sugar through faulty treatment have induced Marot to give up the use of lime and baryta salts, in order to carry out the refining with a minimum of lime ($\frac{1}{3}$ per cent.). Marot boils the solution after having added the lime until its volume has been reduced to one-fifth, expecting thereby to decompose the nitrogenous substances, and to liberate the resulting ammonia.

With regard to the probable success of this process, it is to be observed that soluble lime salts and lactates must remain behind after the purification of the juice by this treatment, and it is by no means proved that all the nitrogen is thereby removed. Analyses of the juices thus treated and of the boiled masses are the only means of judging whether the yield is increased, and whether the method is to be preferred to the ordinary process.

D. B.

Use of Hydrochloric Acid in the Diffusion-process. (*Dingl. polyt. J.*, cxxi, 92).—At several sugar refineries, the so-called "bad pressing," i.e., a more difficult and slow circulation of the sap through the layers has already been noticed during the diffusion, and Erk showed last year how, after a normal working of two months, this bad pressing came on to such an extent, that instead of 125 tons only 42.5 tons of beetroots could be worked in one layer.

For every pan of 3,000 liters of contents or 2,500 kilos. of charge, 1.5 to 2 liters of 40 per cent. hydrochloric acid diluted with an equal bulk of water was added, which at once produced a normal pressing. This action seems to depend on the fact that certain organic substances coagulate, and are rendered insoluble by the acid. D. B.

Myall-wood. By J. MOELLER (*Dingl. polyt. J.*, ccxxi, 153—156).—At the present time a species of wood imported from Australia is largely used in commerce under the above name, and forms a substitute in the manufacture of the well-known briar pipes. At the ordinary temperature, this wood smells very strongly of violets; it is very hard and heavy, and does not split regularly. Its spec. grav. is 1.578. When dried at 100°, it yields 11.25 per cent. of ash containing the following percentage ingredients:—

Silicic acid	0.401
Carbonic acid	43.721
Sulphuric acid	0.488
Phosphoric acid	0.103
Chlorine	0.098
Potash.....	2.621
Soda	2.054
Lime	47.583
nesia.....	3.879

100.898

Deduct the quantity of oxygen
equivalent to the chlorine..... 0.022

100.876 D. B.

Carboazotin, a new Explosive Substance. (*Dingl. polyt. J.*, ccxxi, 94).—According to Cahuc and Soulages, a mixture of—

50—64 parts of potassium nitrate (sodium or lime),	
13—16 „ sulphur,	
14—16 „ tan,	
9—18 „ soot, lampblack, &c.,	
4— 5 „ iron vitriol,	

is heated with a corresponding quantity of water at 110—120°, the liquid cooled, the solid mass dried and brought into forms, &c.

According to the English patent of Faure and Trench, a mixture of 1 part of charcoal, 16 parts of barium nitrate, and 1 part of nitro-cellulose, are made up with water to a pulp, then formed into cakes and dried. D. B.

Manufacture of Yeast. By F. VAN HEUMEN and W. H. VAN HASSELT (*Dingl. polyt. J.*, ccxxi, 451—465).—Yeast is now prepared according to one of the following methods:—

1. *Dutch Method.*—In Holland, a tax is levied on the spirit produced, whereas the coops and apparatus are free from taxes; hence in that country it is advantageous to carry on the fermentation in a

large number of vessels. The raw material is always rye- and barley-malt. These substances are ground to a fine powder, and washed with hot water, until a temperature of about 65° has been reached. The mixture, after the lapse of 1—2 hours, is cooled to 37° with clear brewer's wash, and then to 30 — 32° with water, at which temperatures the yeast is added. The fermentation commences gradually, and goes on so slowly, that the returns and the other insoluble substances are deposited. After three hours' standing the liquid is run off, and pumped into a shallow square vessel, whereby the temperature is lowered to about 20° . The actual fermentation and formation of yeast takes place in this vessel, two layers of yeast being formed, the one on the surface of the liquid and the other at the bottom of the vessel. The clear liquid between the two layers is, after the termination of this fermentation, drawn off and brought back to the first mashing vessel, where its fermentation is completed with that of the returns left behind. The yeast is brought into smaller vessels, where, after depositing, it is sifted, washed, and pressed. The vessels used hold about 2,200 liters, in which 95 kilos. of rye and 95 kilos. of malt are mashed. From 100 kilos. of flour, 10 to 12 kilos. of yeast and 26—28 liters of spirit of 100 p. c. are obtained. The mash obtained varies from 62.5 to 67 per cent.

2. *German Method.*—In Germany, spirits are not taxed, but vessels and apparatus taxed very heavily, which circumstance renders it necessary to occupy as little space as possible for fermenting vessels and other apparatus. Besides rye and malt, maize is also used, which, on account of its hardness, requires to be boiled in water for 1—2 hours before it can be used. The hot maize is added to the mash of rye and malt at a temperature of 65° , and after saccharification cooled to 37° . The mass is then run into the fermenting vessels, cooled with clear wash, and treated with yeast. After the fermentation has terminated, the mass is separated from the returns by sifting, and mixed with water. The mixture is again filtered and washed, and the yeast, after settling, is pressed, while the cold mash on the top of the yeast is again pumped into the fermenting vessels and allowed to stand for two days. After this the fermentation is finished. The liquid can now be distilled off. In one hectoliter of space, 13.88 kilos. of flour (70 p. c. maize and rye and 30 p. c. malt) are mashed; 50 litres of wash are required for cooling purposes, and the mash obtained is equal to 67 p. c. of extract. 100 kilos. of raw material give from 9 to 10 kilos. of yeast and 28 to 30 liters of spirits of 100 p. c.

3. *Method with Clear Mash.*—By this method a product of great purity and strength is obtained which has proved to form an excellent article in panary fermentation, and is of great importance to bakers, who very often have only a limited space at their disposal, and require a substance which raises the dough very readily. 20 p. c. of rye, 30 p. c. of maize, and 50 p. c. of barley-malt, are mashed in a vessel, at the bottom of which a perforated plate is placed, under which a cock is fixed for letting off the liquid. After the saccharification is finished, the clear mash is drawn off at the bottom of the vessel, and the returns are washed with hot water. The filtrate is then cooled to 27° , and the yeast added. The mash, after fermentation, is pumped

into a shallow vessel, where the yeast is deposited. The clear mash is then taken back into the fermenting vessel, and the yeast obtained is washed and pressed. For 1 kilo. of grain about 7.5 liters of mash are obtained, equal to about 56 p. c. of extract. The yield of yeast is calculated at 9 p. c., that of spirit (100 p. c.) at 24—25 p. c.

With regard to the raw material, the method (2) is the most profitable, as less malt is required and the composition of the mash can be chosen in such a manner that the grain which is the cheapest at the time shall predominate in it.

With regard to the apparatus used and the space required for fermentation, the method (1) is the most expensive, and suitable only for places where no duty has to be paid on vessels and other apparatus. Regarding the labour attached to the three methods, it is shown that methods (1) and (3) require only a very small staff of workmen. Method (2) requires more workmen. The largest yield of yeast is obtained from method (1); most spirit from (2); this difference is due to the composition of the mash, and can be decreased by mashing less maize and more rye in method (2). The reason why the method (3) gives a low percentage of spirit is that the extraction of starch from the grain is never effected completely with malt alone, but that the process is continued when the mash is allowed to ferment with the returns, as is the case with methods (1) and (2). In the working of method (3), however, the clear mash is alone employed, so that a portion of the starch is not dissolved, but remains behind with the returns when sifted. Method (1) gives the finest quality of spirit, its purity being due to the absence of maize, whose fatty and oily ingredients give the spirit a bad taste, which is difficult to remove. The small yield of yeast in method (3) is due to an analogous cause. The mash obtained from methods (1) and (2) is generally turbid when it is pumped from the fermenting vessel into the boxes. This turbidity is caused by admixtures of albuminous substances, finely divided cellular tissues, &c., which are probably dissolved during the fermentation and thus increase the yield of yeast. The yeast obtained from method (3) is perfectly white and very pure.

The authors experimented on the above-mentioned methods with the view of discovering a new method, combining with method (3) all the advantages of the other two methods. The following are the results obtained. In the first place, the grain is well trimmed and ground into a fine powder. In order to prepare the mash, two-thirds maize and rye and one-third malt are used. After having boiled the maize and rye with steam, the mixture is saccharified with malt, and the mash pumped into filter-presses. By boiling the former substances with steam before using them, it is possible to increase the quantity of rye used, and to work with larger quantities of the latter. The advantages which are gained by using filter-presses are, that the returns require less water for washing purposes, and therefore yield a clearer and more concentrated mash. The returns, after pressing, are washed with hot water. The clear mash is cooled, brought into the fermenting vessel, the necessary quantity of wash added, and the whole treated with yeast. By passing filtered air through the mixture, a more ready and

a larger formation of yeast is resulted. During the time allowed for fermentation, the filter-presses are opened, the pressed cakes taken out, put into boxes, treated with water, and boiled with dilute acid in a copper still. The reason why acid is used is, that it extracts a larger quantity of product from the returns than water alone. After one hour's boiling the still is opened, and the resulting mash brought into the filter-presses. The clear mash is cooled, mixed with water, and added to the fermenting mash. After the end of the fermentation, the clear mash is syphoned off and pumped into retorts, where the washings are redistilled, while the residual yeast is washed and pressed. The returns remaining in the press are dried as completely as possible, and are then ready for use.

The advantages of this method are that :

- (1.) All kinds of grain (and probably even potatoes) can be worked up in various proportions, and the addition of malt can be decreased.
- (2.) By working the clear concentrated mash, the space for fermentation is thoroughly utilised.
- (3.) The shallow cooling and fermenting vessels are not required.
- (4.) The mash becomes clear without being boiled.
- (5.) The yield of yeast and spirit is high, the yeast pure and white, and the spirit from rye of a fine quality.
- (6.) The costs for labour, &c., are but slight.
- (7.) The consumption of coal is small.

D. B.

Manufacture of Glue. By B. TERNE (*Dingl. polyt. J.*, cccxi, 251—258).—The author contradicts the assertion of Gintl, that "the quality of the glue is not impaired by the use of high pressure steam;" on the contrary, he finds that the inferiority of the product is directly proportional to the pressure of the employed steam, till at length all the gelatin is destroyed. The same material which at a pressure of 10 to 20 lbs. per square inch yields a tolerably good product, yields at a pressure of 30 lbs. or over (duration of boiling being in both cases equal) a perfectly white substance quite innocent of gelatin. The author states that the liquors obtained on steaming the slaughter-house refuses may, besides being valuable for glue production, be looked upon as a source of ammonia. Seeing that a high temperature is injurious to the gelatin in the extractive liquors to be boiled down, the author proposes the use of vacuum-pans for this boiling down process. It is asserted that a glue factory is no more prejudicial to the health of a neighbourhood than a starch or yeast factory. The raw materials used for glue-making in the United States are comprised in two classes—(I) Slaughter-house refuse and remains; (II) Refuse of tanneries. The preparation of bone-glue by extraction of the mineral constituents of bones by means of hydrochloric acid, thus leaving the gelatin, pays only in those neighbourhoods where hydrochloric acid is to be had cheap.

Use of Slaughter-house Refuse.—According to their value as a source of glue, the varieties of the raw materials are arranged as follows:—

- (1) Feet of oxen; (2) pig's feet; (3) feet of calves and sheep;
- (4) fresh bones; (5) heads of sheep and oxen. The raw material is

freed from blood as much as possible, and reduced to as fine a condition of division as practicable, the flesh being torn to pieces and the bones broken by a suitable machine, and then washed free from dirt and blood. The matter is then ready for the boiling operation in the ordinary course, but the author here introduces a process for bleaching by means of sulphurous acid. This is done in wooden vats, closely covered, and a saturated sulphurous acid solution is used. The time required for the bleaching depends greatly upon the condition of the material. By means of this important process, an extractive liquor is obtained nearly as clear as water, which by evaporation in the vacuum pan yields a glue unsurpassed for clearness and lustre by the very first qualities. The bone-fat is likewise clearer and free from objectionable odour, and commands a considerably improved price. In order to prepare the concentrated sulphurous acid solution, a sulphur-burner, from the roof of which a stoneware pipe passes, supplies a reservoir with sulphurous oxide gas. This gas afterwards passes up a coke tower (connected with the upper part of the reservoir by a series of short stoneware pipes), and meets a slow current of water, which trickles down amongst the coke, and is supplied by a cistern from above. The resulting concentrated solution accumulates in the reservoir below. The action of the acid is very characteristic. The particles of skin and flesh swell out, and finally assume the lustre of silk and the transparency of gelatin. The mass is also rendered much more porous, and thus can be far more quickly converted into glue. The boiling process then follows, and the advantage of the previous bleaching is made evident in the short time and low pressure required in this boiling, which gives a good concentrated liquor. The melted fat is removed by taps. The liquor, free from fat, is now passed through a filter containing bone-charcoal, but the author believes that a filter-press, manufactured by Wegelin and Hübner, of Halle, would answer the purpose better. From the filter the liquor passes to the vacuum-pan, where it is evaporated down till of such a consistency that the resulting glue may be easily cut, or if cast in moulds, easily detached therefrom and in a short time. For the pouring, plates of tinned sheet iron are generally used, but recently glass tables have been introduced, by the use of which an extraordinary gloss is conferred upon the glue. These tables are, however, liable to frequent breakage. When moulds are used, they are cooled down by cold water and ice, and when the temperature falls to within 0° and 5° , the glue may be removed. A process has been recently patented for America in which benzene is used for removing the fatty portions of the raw material for glue-making.

W. S.

Logwood Inks. By E. U. VIEDT (*Pharm. J. Trans.* [3], vi, 1004).—Inks prepared from logwood are of four classes, viz., with logwood and chrome, with alum, with copper, or with iron. Runge's ink, prepared from logwood with a small quantity of potassium chromate, is good and cheap, easily penetrating the paper; but on exposure to air it deposits black flakes, leaving a colourless liquid above. This may be prevented by the addition of a little sodium carbonate; the following ink is therefore recommended. Dissolve 15 parts of log-

wood extract in 900 of water; leave the liquid to deposit and decant; heat and add 4 parts of crystallised sodium carbonate; lastly add drop by drop a solution of 1 part of potassium chromate in 100 of water. Inks prepared from chrome-alum have little depth of colour. Under the influence of air, reaction takes place between the metallic salts and the colouring matter; sulphuric acid is therefore added, and this attacks the pens. If metallic salts are used, cupric sulphate is preferable.

One of the best formulas for this kind of ink is the following, given in proportions for a manufacturing scale:—20 kilograms of extract of logwood are dissolved in 200 litres of water and the solution clarified by subsidence and decantation. A yellowish-brown liquid is thus obtained. In another vessel 10 kilograms of ammonia-alum are dissolved in 20 litres of boiling water; the two solutions are mixed, there being also added 200 grams of sulphuric acid, and finally $1\frac{1}{2}$ kilogram of sulphate of copper. The ink should be exposed to the air for a few days to give a good colour, after which it should be stored in well-corked bottles.

Boettger gives the following formula:—30 grams of extract of logwood are dissolved in 250 grams of water; 8 grams of crystallised carbonate of soda and 30 grams of glycerin of density 1.25 are added; and lastly, 1 gram of yellow chromate of potassium and 8 grams of gum arabic reduced to a powder and dissolved in several grams of water. This ink does not attack pens, does not mould, and is very black.

E. W. P.

Carbon Disulphide as an Antiseptic. By HUGO SCHIFF (*Deut. Chem. Ges. Ber.*, ix, 828).—Cocoons of silkworms which had been killed by exposure to the vapours of carbon disulphide underwent no change during six months' keeping in flasks in the laboratory.

The bodies of some pigs which had been used for physiological experiments were put into a stoppered vessel with a few c.c's. of carbon disulphide in 1869, and have been perfectly preserved without decomposition. The same result was obtained with a lizard 35—45 centimeters long, which had been suffocated accidentally in 1869, and was bottled whole. In this case a small quantity of liquid collected at the bottom of the vessel, and the green hue of the skin became a dirty greyish-green, but not the slightest putrefaction occurred.

Similar results were obtained with the intestines of poultry immersed in water in 1872, with a little carbon disulphide in a bottle with a greased stopper; with a lump of beef weighing 200 grams; and with the body of a finch killed by paraconine. The beef yielded a normal flesh fluid, and was eaten by a dog without hesitation, even after several months.

C. R. A. W.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

III.—*Study of Hydrogen Dioxide and of certain Peroxides*—(continued from page 24).

By T. FAIRLEY, F.R.S.E.

VII. ON SODIUM DIOXIDE.

IN alcoholic solutions this substance may be precipitated by addition of hydrogen dioxide, in a manner closely resembling the precipitation of barium, strontium, and calcium dioxides, by the same reagent, from aqueous solutions of their hydrates. Thus, if to a solution of sodium hydrate containing about 20 per cent. of NaHO we add a solution of hydrogen dioxide containing about 5 per cent. H_2O_2 , and then common alcohol of 80 per cent. in moderate excess, there is rapidly—often immediately, formed a crystalline precipitate of hydrated sodium peroxide. In this preparation it is better to have excess of alkali, rather than of the dioxide. The precipitate should be rapidly separated from the liquid by filtration through a ribbed paper filter, or, still better, a cloth filter, as the crystals gradually decompose when suffered to remain in the liquid.

The crystals of this sodium peroxide have the beautiful pearly lustre characteristic of many hydrated peroxides, and consist of sodium dioxide with eight atoms of water of crystallisation. They do not contain any alcohol. They are identical with the crystalline hydrate described by Vernon Harcourt*, and obtained by the evaporation of the solution of anhydrous sodium dioxide prepared by heating sodium in a current of oxygen. Thus they lose water by exposure over sulphuric acid in a vacuum; and on exposure to the air for a few days they rapidly lose their brilliancy, owing to formation of sodium carbonate from absorption of carbon dioxide and evolution of oxygen.

When considerable quantities are operated on, crystals may sometimes be obtained of considerable magnitude in large mica-like plates. This is observed more especially in cold weather. These plates are transparent, flexible, and can be split with the knife in the same manner as mica. They may be formed from smaller crystals, uniting together in the same way as shown by ice in the process of regeneration.

* *Chem. Soc. J.*, xv, 287.

As showing the influence of various proportions of reagents, the following experiments may be quoted :—

(I.) On mixing—

10 c.c. NaHO solution (20 per cent.)
 4 c.c. H_2O_2 „ (5 per cent.)
 20 c.c. alcohol (80 per cent.).

an abundant precipitation of the dioxide was obtained.

(II.) 10 c.c. of the same NaHO solution
 7·5 c.c. „ H_2O_2 „
 22 c.c. „ alcohol

also gave an abundant precipitate of the dioxide, and the precipitation appeared to be facilitated by addition of a little more sodium hydrate.

(III.) 10 c.c. of the same NaHO solution
 20·4 c.c. „ H_2O_2 „
 60 c.c. „ alcohol

gave no precipitate, but only a slight opalescence.* The further addition of alcohol also failed to give a precipitate, which was, however, immediately obtained on addition of sodium hydrate.

These experiments show that while excess of sodium hydrate does not interfere with the precipitation, excess of the hydrogen dioxide interferes with or even prevents it. This may be due to the formation of a double peroxide of sodium and hydrogen soluble in alcohol. It is also to be observed that oxygen is much more freely evolved in presence of excess of the hydrogen dioxide. This may arise either from the decomposition of the unstable double peroxide, if such be formed, or else according to the equation—



By heating this dioxide alone, about seven-eighths of the water are given off and all the peroxide oxygen, and by heating it with silica, or in a current of carbon dioxide, all the water and peroxide oxygen are expelled. The latter, therefore, form convenient processes for the analysis of the dioxide.

In the following analyses the oxygen was generally determined in acid solutions by means of decinormal potassium permanganate :—

I. 0·1 gram required 9 c.c. of permanganate = 0·0072 oxygen, corresponding to 7·2 per cent.

II. 0·0705 required 6·35 c.c. permanganate = 0·00508 oxygen, corresponding to 7·2 per cent.

* On exposing this liquid to cold, it deposits a small quantity of fine crystalline needles. These, though very different in appearance and form from the crystals obtained by Expts. I and II, have the same composition.

- III. 0.1135 evaporated with hydrochloric acid gave 0.0592 gram sodium chloride, and required 10.2 c.c. of decinormal silver nitrate, corresponding to 27.85 per cent. of Na_2O .
- IV. 0.1009 gram decolorised 9.1 c.c. permanganate = 0.00728 oxygen, corresponding to 7.21 per cent.
- V. 0.854 gram decolorised 77 c.c. permanganate = 0.0616 oxygen, corresponding to 7.21 per cent.
- VI. 0.924 gram decolorised 83.2 c.c. permanganate = 0.06656 oxygen, corresponding to 7.21 per cent.
- VII. 0.2 gram boiled with 10 c.c. normal sulphuric acid neutralised 1.8 c.c. = 0.0559 sodium oxide, corresponding to 27.95 per cent.
- VIII. 0.3265 gram heated with silica gave 0.2125 gram water, corresponding to 65.09 per cent.
- IX. 0.4157 gram heated in a current of pure dry carbon dioxide gave water 0.2689 gram, corresponding to 64.68 per cent., and sodium carbonate 0.19875 gram, corresponding to sodium oxide 27.96 per cent.

These results agree with the formula $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, as the following percentages show:—

	Found.								
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Na ₂ O	—	—	27·85	—	—	—	27·95	—	27·96
O	7·20	—	—	7·21	—	—	—	—	—
H ₂ O	—	—	—	—	—	—	65·09	—	64·68
	Calculated.						Mean found.		
Na ₂ O	62	—	27·97	—	—	—	—	—	27·92
O	16	—	7·20	—	—	—	—	—	7·20
8H ₂ O	144	—	64·83	—	—	—	—	—	64·88
	222	—	100·00	—	—	—	—	—	100·00

VIII. ON NEW OXIDES AND COMPOUNDS OF URANIUM.

Uranium Tetroxide.

On addition of pure dilute hydrogen dioxide to solution of uranic nitrate or acetate, a yellowish-white precipitate is formed somewhat lighter in colour than freshly prepared uranic hydrate. In presence of excess of uranium salt the precipitate is very stable, and may be dried at 100°C . without losing oxygen. If the hydrogen dioxide is in excess, oxygen is evolved during the filtration of the precipitate from the liquid, especially if the latter is not quite cold. In no case

has any lower oxide than that corresponding to the empirical formula UO_4^* been obtained.

The presence of excess of salts of sodium, potassium, barium, calcium, and probably many others, prevents the precipitation of uranium by hydrogen dioxide, and hence the new oxide is either not obtained at all, or slowly and with difficulty, by mixing an acid solution of barium dioxide with the solution of a uranic salt.

A moderate excess of strong hydrochloric, nitric, or sulphuric acids also delays or prevents the precipitation, and sulphuric acid is much more powerful in this respect than any other substance whose action I have observed.

The oxide when dried at 100° is a yellowish-white powder, soluble, especially on heating, in strong hydrochloric acid with evolution of chlorine. A mixture of the oxide with hydrochloric acid readily dissolves gold.

On exposure to heat, this oxide if finely divided, undergoes a very remarkable decomposition. At a comparatively low temperature, much below redness or the softening point of the more readily fusible glass, a red glow passes through the mass, oxygen is freely given off, and the residue contains a considerable proportion of green oxide of uranium.

On treating this oxide with alkaline hydrate, one portion of the uranium is precipitated as ordinary uranic hydrate, and the other enters into solution to form a salt or new oxygen compound with the alkali. These compounds may be viewed as derived from an acid of uranium analogous to perchromic acid, and, if so, would be similarly named as salts of peruranic acid.

The fact of the precipitation of the oxide from acid solutions shows, that unless we attribute to hydrogen peroxide the character of an acid, these compounds cannot be regarded as compounds of hydrogen dioxide. I do not, however, consider this view as untenable on that account, and have borne it in mind throughout the study of this class of compounds. According to this view the salts to be afterwards described are double peroxides.

Neither hypochlorites nor permanganates, nor ozone in acid, neutral or alkaline solutions, nor any other oxidising agents which I have hitherto examined (with the exception of hydrogen dioxide, alkaline peroxides, &c.) give any higher oxidation products with uranic salts. Hypochlorites and permanganates in acid liquids decompose this oxide in common with other peroxides.

Out of a very large number of experiments, the following may be quoted in illustration of the influence of varying proportions of reagents used, the completeness of the precipitation of uranium under

* $\text{U} = 240$.

suitable conditions, and the composition as proved by synthesis of the oxide formed.

On mixing :—

(I.) Uranium acetate solution 100 c.c. containing 4.877 grams UO_3 .

Hydrogen dioxide „ 38 c.c. „ 1.064 „ oxygen

an abundant precipitate was obtained. The filtrate contained no uranium (as proved by evaporation to dryness and also by testing with potassium ferrocyanide), but it contained the excess of H_2O_2 and abundance of free acetic acid.

(II.) Uranium *nitrate* solution 90 c.c. containing 1.72 grams UO_3 .

Hydrogen dioxide solution 10 c.c. containing 0.152 gram oxygen.

After making up the liquid to 200 c.c. and allowing the precipitate to settle, the clear liquid on testing with ferrocyanide showed uranium in solution. I therefore added to the whole bulk 13 c.c. of normal sodium hydrate solution containing 0.52 gram NaHO , and after thorough mixing and allowing the precipitate to settle, the clear liquid was again tested. It had an acid reaction, and showed no uranium by evaporation or on testing with ferrocyanide. After filtering and washing the precipitate, I observed that 1 c.c. of the normal sodium hydrate solution was sufficient to change the reaction of the filtrate from acid to alkaline, and that it contained hydrogen dioxide, as tested by permanganate, equivalent to 0.056 gram oxygen. The precipitate dried at 100°C . weighed 2.034 grams, and the formula $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ requires that it should weigh 2.0293 grams.* The formula also requires that it should contain 0.0956 gram of peroxide oxygen, and this experiment gives 0.096 gram. This experiment shows that the precipitation of uranium in nearly neutral solutions is complete, and that the oxide precipitated has no acid reaction.

(III.) Uranic nitrate solution 50 c.c. containing 0.93 gram UO_3 .

Hydrogen dioxide solution 6 c.c. containing 0.0912 gram oxygen.

On making up the solution to 100 c.c. and filtering, 25 c.c. of the filtrate required 12.2 c.c. permanganate, showing that the excess of hydrogen dioxide in the filtrate contained oxygen amounting to 0.03904 gram. This gives peroxide oxygen contained in the precipitate 0.05216 gram, while the formula requires 0.052 nearly. In this experiment, nearly the whole of the uranium was precipitated, only a minute portion being kept in solution by the acid set free from the

* The equation representing the formation of this oxide may be written :—



nitrate. To determine this amount, another portion of 25 c.c. (one-fourth of the filtrate), evaporated to dryness and ignited, gave .009 of residue, consisting chiefly of UO_3 , and to determine the acid set free, I found that 25 c.c. of the filtrate required 20 c.c. of decinormal sodium hydrate, proving that the total filtrate contained 0.504 gram HNO_3 . The formula $\text{UO}_3 \cdot \text{N}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$, would give 0.407 gram, and the examination of the crystalline salt from which the above solution was prepared, showed that free nitric acid was present, the crystals no doubt having been formed in a strongly acid liquid. The free acid contained in the hydrogen peroxide used was very minute, corresponding to 1.8 c.c. of decinormal sodium hydrate solution.

(IV.) To show that there is, practically, no decomposition of hydrogen dioxide in such liquids as the above during the time of an experiment, I took 2 c.c. of the hydrogen dioxide used in Experiment 3, and 10 c.c. of the uranic nitrate solution, and after allowing the mixture to stand over four hours titrated with permanganate. There was decolorised 38 c.c. = .0304 oxygen, corresponding to 3.23 per cent. of real dioxide—exactly the percentage found in the dioxide titrated directly. This proves that, at ordinary temperatures, uranic oxide does not induce decomposition in the same manner as chromic and permanganic acids acting on hydrogen dioxide.

The following analyses have been made of this oxide after drying at 109°C .:—

- I. 0.279 gram ignited till its weight remained constant, gave 0.228 gram U_2O_5 , corresponding to 70.07 per cent. of uranium, or 84.08 per cent. of UO_3 .
- II. 0.329 gram treated with dilute sulphuric acid and titrated with permanganate, decolorised 19 c.c. = .01552 gram oxygen, corresponding to 4.71 per cent. of oxygen.
- III. 0.336 gram decolorised 19.7 c.c. permanganate solution = .01576 gram oxygen, corresponding to 4.69 per cent.
- IV. 0.336 gram decolorised 20 c.c. permanganate = 0.016 gram oxygen, corresponding to 4.76 per cent.
- V. 0.34 gram decolorised 20 c.c. permanganate = 0.016 gram oxygen, corresponding to 4.705 per cent.
- VI. 0.34 gram of this oxide decomposed by ignition and then dissolved in dilute nitric acid and titrated after addition of ammonia and acetic acid with standard solution of pure sodium phosphate (1 c.c. = 0.01858 gram UO_3 = 0.01548 U), required 15.5 c.c. = .2879 UO_3 , corresponding to 70.56 per cent. uranium, or 84.67 per cent. UO_3 .
- VII. 0.7 gram decolorised 41.3 c.c. permanganate solution = 0.3304 gram oxygen, corresponding to 4.72 per cent. of oxygen.

- VIII. 0·81 gram decolorised 48 c.c. permanganate = 0·384 gram oxygen, corresponding to 4·74 per cent.
- IX. 0·82 gram, after decomposition in acid solution by permanganate, was treated in the flask with granulated zinc and dilute sulphuric acid to reduce the uranium to uranous salt. (The liquid should scarcely cover the zinc, and the reduction is finished within 30 minutes more or less according to the proportions used. The liquid is then diluted, decanted clear or filtered, the zinc washed, and the washings added to the liquid, and the titration proceeded with after addition of dilute sulphuric acid.) There was decolorised in this case 48 c.c. of decinormal permanganate solution (1 c.c. = 0·008 gram oxygen = 0·12 gram uranium) = 0·576 gram uranium, corresponding to 70·24 per cent. of uranium, or 84·28 of UO_3 .
- X. 0·81 gram titrated with permanganate required 48 c.c. permanganate = 0·384 gram oxygen, corresponding to 4·74 per cent. After reduction, it required 47·5 c.c. permanganate = 0·57 gram uranium, corresponding to 70·37 per cent., or 84·44 UO_3 . These numbers give water by difference as 10·82 per cent.
- XI. 0·81 gram gave 0·089 gram water, corresponding to 10·98 per cent.
- XII. 0·38 gram gave 0·04 gram water, corresponding to 10·52 per cent.

The following analyses have been made of the *air-dried* oxide prepared by pressure between folds of filter-paper:—

- XIII. 0·958 decolorised 51 c.c. permanganate = 0·0408 oxygen, corresponding to 4·25 per cent.
- XIV. 0·2572 heated in a current of dry carbon dioxide gave off 0·05 gram water = 19·44 per cent., and 0·16 gram oxygen. The residue contained a certain proportion of green uranous oxide, so that when dissolved in sulphuric acid it reduced 6·25 c.c. of permanganate solution = 0·05 gram oxygen. Deducting this oxygen from the total given off, we have 0·11 gram due to the change of UO_4 into UO_3 , corresponding to 4·23 per cent. The residue weighed 0·191 gram, and adding the above oxygen = 0·196 gram UO_3 , corresponding to 76·20 per cent.

These numbers agree with the empirical formulæ:—

For the oxide dried at 100° C. $\text{UO}_4 \cdot 2\text{H}_2\text{O}$
 And the air-dried oxide $\text{UO}_4 \cdot 4\text{H}_2\text{O}$

as the following comparisons show:—

The oxide dried at 100° C.

	Calculated.	Found.												Mean.
		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	
U ..	240	70.59	84.71	—	—	84.67	—	—	84.28	84.44	—	—	—	84.37
O ₂ ..	48	14.12												
O ..	16	4.70	4.71	4.69	4.76	4.705	4.72	4.74	4.74	4.74	—	—	—	4.72
2H ₂ O ..	86	10.59	—	—	—	—	—	—	—	10.82	10.98	10.52	—	10.77
	840	100.00												99.86

The air-dried oxide.

	Found.				Mean.
		XIII.	XIV.		
U	240	—	76.20	76.20	76.20
O ₂	48	—	—	—	—
O	16	4.25	4.23	4.24	4.24
4H ₂ O ..	72	—	19.44	19.44	19.44
	376	—	—	—	—
	100.00	—	—	—	99.88

The decomposition of this oxide by alkaline hydrates and the study of the alkaline-compounds corresponding to it, lead to the adoption of a formula of thrice the molecular weight of the above, viz. :—



According to this view, it is the uranium-salt of peruranic acid.

Anhydrous Uranium Tetraoxide.

When uranic nitrate solution is added to a mixture of hydrogen dioxide and large excess of sulphuric acid, no precipitate is obtained. On standing, however, a sufficient length of time, sometimes after a week, sometimes several weeks, a precipitate is slowly formed, which, as yet, I have only obtained in very small quantity. It is almost white in colour, generally heavy and crystalline, and is much more inert than the hydrated oxide previously described. Thus it is difficult to decompose it with permanganate, even in presence of large excess of sulphuric acid. On applying heat, the permanganate is slowly decolorised. The titration with permanganate is much facilitated by mixing the oxide in a mortar with a little strong alkaline hydrate solution, and then adding excess of sulphuric acid.

When carefully dried, this oxide gives off no moisture on heating alone. On heating it with hydrochloric acid, chlorine is evolved.

The analyses of this and the following compound must be regarded as provisional, pending attempts to obtain them in larger quantity.

- I. 0.0602 decolorised 3.95 c.c. permanganate
 = .00316 oxygen, or 5.24 per cent.
 ,, gave .057 UO_3 , or 94.68 per cent., corresponding to 78.94
 per cent. of uranium.
- II. 0.154 decolorised 10 c.c. permanganate = .008 oxygen or 5.19 per
 cent., and gave .146 UO_3 , or 94.8 per cent., corresponding
 to 79 per cent. of uranium.

These numbers agree with the formula UO_4 .

		Calculated.	Found.		Mean.
			I.	II.	
U 240	78.95	94.78	94.8	94.79
O ₃ 48	15.79			
O 16	5.26			
	<hr/> 304	<hr/> 100.00		<hr/> 5.19	<hr/> 5.21
					<hr/> 100.00

Higher Uranium Oxides.

I have not obtained the oxide U_2O_5 in a pure state, or free from moisture. I have, however, determined the ratio of the uranium to

the oxygen in precipitates obtained by the slow decomposition of liquids prepared with a view to the isolation of peruranic acid (double peroxide of uranium and hydrogen, $\text{UO}_6 \cdot x\text{H}_2\text{O}$?).

5.04 grams ($= \frac{1}{16}$ atom in gram units) of pure crystallised uranic nitrate, were dissolved in the smallest possible quantity of water, and added gradually to a mixture of 20 c.c. of strong nitric acid of 60 per cent., and 45 c.c. hydrogen dioxide of 2.4 per cent. The liquid was made up to 75 c.c., and allowed to stand overnight. There was a very slow evolution of oxygen and deposition of a quantity of crystalline precipitate, which was collected and dried on clean bricks.

It was found to be completely soluble on triturating with sodium hydrate solution (20 per cent.), forming a liquid resembling in colour and characters the solution of the red-sodium salt to be afterwards described (p. 139).

Different portions of the precipitate gave the ratio—

$$\left. \begin{array}{l} \text{UO}_3 : \text{O} :: .489 : .04 \\ .489 : .0408 \\ .489 : .039 \end{array} \right\} = 12 : 1$$

This corresponds to the ratio of uranium to peroxide oxygen = 10 : 1 as required by the formula $\text{U}_2\text{O}_6 \cdot x\text{H}_2\text{O}$.

Attempts made to isolate the highest of these oxides corresponding to the salts have hitherto been unsuccessful. I shall, however, continue my efforts by application of very low temperatures for the isolation of the solid or liquid body, $\text{UO}_6 \cdot x\text{H}_2\text{O}$.

The decomposition of acid liquids containing uranic oxide and hydrogen dioxide in the proportions required by the formula UO_6 , varies considerably according to the temperature, the acid used, and other circumstances. It appears most apt to proceed to the limit of uranium tetroxide in the case of hydrochloric acid,* and least so in the case of sulphuric acid.

Ammonium Peruranate.

(Double Peroxide of Uranium and Ammonium.)

This salt is precipitated on addition of alcohol to uranic solutions to which hydrogen dioxide and ammonia in excess has been added.

On mixing a solution of 2.52 grams of crystallised pure uranic nitrate containing 1.2 gram uranium, 10 c.c. of hydrogen dioxide of 3.23 per cent., and then ammonia solution in excess, the precipitate at first formed was dissolved. Oxygen was also evolved, though to a less extent than in the preparation of the potassium salt. On addi-

* A bottle exploded in my hands in which this mixture had stood overnight.

tion of strong alcohol, the greater portion of the uranium was gradually precipitated. After standing one hour, the precipitate was collected on the filter.

Another experiment made by mixing 50 c.c. of uranic nitrate solution containing 0.774 gram of uranium with 10 c.c. of the same hydrogen dioxide and excess of ammonia gave, on addition of alcohol, and standing for one and a half hours a much less successful result. Excess of hydrogen dioxide therefore interferes with the precipitation of this compound.

The salt thus prepared is an orange-yellow precipitate readily soluble in water. In the dry solid state it is less affected by exposure to the air than the corresponding potassium or sodium compounds. It is the only ammonium salt that I have as yet obtained. Its solutions are precipitated by sodium and potassium hydrates, ordinary uranic hydrate being separated and sodium or potassium peruranates remaining in solution. Its solution gives precipitates with the solutions of most of the metals.

On heating the dry salt it glows like tinder and leaves a residue containing uranic and lower oxides of uranium.

The following analyses have been made:—

- I. .372 gram salt titrated with permanganate required 27.3 c.c. = .0218 gram oxygen, corresponding to 5.86 per cent.
- II. .25 gram salt ignited gave residue U_3O_8 .173 gram = .176 UO_3 , corresponding to 70.4 per cent. UO_3 , or 58.67 per cent. uranium.
- III. .24 gram ignited, the residue dissolved in nitric acid, required, after addition of ammonia and acetic acid, 9.2 c.c. standard sodium phosphate solution to precipitate the uranium = .01548 \times 9.2 gram uranium = .1425 gram, corresponding to 59.35 per cent.
- IV. .41 gram dissolved in water required 10.2 c.c. decinormal sulphuric acid = 0.01734 gram NH_3 , corresponding to 4.22 per cent.

N.B.—The change of colour of the solution may be used as an index of the end-reaction and corresponds to the tests shown by litmus paper.

- V. .82 gram distilled with sodium hydrate and the ammonia estimated in the distillate required 20 c.c. standard acid = .034 NH_3 , corresponding to 4.15 per cent. ammonia.
- VI. .205 gram decolorised 15 c.c. permanganate = .012 gram oxygen, corresponding to 5.85 per cent.
- VII. .205 gram decolorised 15 c.c. permanganate = .012 gram oxygen, corresponding to 5.85 per cent.

These results agree with the formula—



as the following comparisons show :—

			Found.							
			Calculated.	<div> <div>I. II. IV.</div> <div>III. V. VI. VII.</div> </div>						
U ₂	480	58.54								
* O ₁₀	160	19.51								
† (NH ₄) ₂	36	4.39								
8H ₂ O	144	17.56								
			Difference							
	<u>820</u>	<u>100.00</u>								

The experimental numbers give the ratios—

Weight of uranium present : oxygen estimated by permanganate,
10 : 1 = 480 : 48.

Weight of uranium present : to ammonium,
40 : 3 = 480 : 36,

results which agree with the above formula.

Regarded as a double peroxide of uranium and ammonium, the formula of this compound becomes 2UO₄ . (NH₄)₂O₂ . 8H₂O. In this point of view this body may indicate the possible existence of ammonium peroxide. Attempts made to isolate this compound have hitherto failed, though I have observed that the smell of a mixture of concentrated hydrogen peroxide and ammonia is peculiar, and I have also obtained a crystalline double peroxide of silver and ammonium. I am therefore not without hopes of success in the isolation of ammonium peroxide.

Sodium Peruranate, UO₆ . 2Na₂O . 8H₂O.

(Double Peroxide of Uranium and Sodium, UO₄ . Na₂O₄ . 8H₂O.)

This compound is readily obtained by dissolving ordinary uranic hydrate or hydrated uranic tetroxide in sodium hydrate solution by addition of excess of hydrogen dioxide. It is well to use excess of alkaline hydrate, so as to avoid the formation of a second salt containing more uranium than the above.

If strong solutions be used, the salt crystallises out in a few hours in the form of yellow needles, sometimes grouped in star-like clusters. If more dilute solutions be used, the salt may be readily separated in crystalline needles or plates by addition of a little alcohol, in which it is much less soluble than sodium peroxide.

When freshly prepared this compound has a beautiful golden lustre.

On exposure to the air, it slowly effloresces with absorption of carbon dioxide and loss of oxygen. It is, however, much less affected by exposure to the air than pure sodium peroxide: an exposure of days in the one case producing little more effect than that of as many hours in the other.

It gives off a proportion of oxygen amounting to three atoms in the above formula in contact with solutions of acidified permanganate, alkaline hypochlorites, and other unstable oxygen compounds.

It gives precipitates with solutions of most of the metals. These precipitates are dissolved or modified by addition of acetic acid.

When heated alone it gives off oxygen gas equal to three atoms in the above formula and about three-fourths of its water, amounting to 17 per cent.

When heated in a current of carbon dioxide it gives off the same proportion of oxygen and all its water, amounting to 24 per cent.

The hydrochloric acid solution of the ignited salt does not dissolve gold, whereas that of the unchanged salt readily does so.

The solution of this salt is not completely decomposed by boiling, either alone or with addition of ammonia.

A solution containing 0.9565 gram boiled with excess of ammonia, and the liquid further left overnight to evaporate on the water-bath, gave a dry residue which was still entirely soluble in water, and on addition of dilute sulphuric acid decolorised 28 c.c. permanganate, showing that about one-third of the peroxide oxygen still remained in solution. During the boiling a precipitate of crystalline scales was observed.

The following experiments may be quoted relating to the preparation of the salt:—

Uranic nitrate solution containing 0.929 gram uranic oxide, dissolved in 50 c.c. of water, was mixed with 10 c.c. of hydrogen dioxide of 3.2 per cent. and excess of sodium hydrate solution. A portion of uranic oxide remained undissolved.

A solution containing half the above quantity of uranic oxide, 0.4645 gram, was mixed with 10 c.c. of hydrogen dioxide of 3.2 per cent. and 2 c.c. of 10 per cent. sodium hydrate solution added. Perfect solution of the uranium took place, and on addition of alcohol there was precipitated first a red crystalline salt and afterwards the yellow salt.

The salt was prepared for analysis by pressure between folds of filter paper. If the filter on which the crystalline precipitate, separated by alcohol, has been collected be spread out on a dry brick, it is easy to dry the salt rapidly. If the wet precipitate be left on the filter in the ordinary way to drain a considerable proportion of the salt may be lost by re-solution, especially in warm weather.

The following analyses have been made :—

- | | |
|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1st preparation. | I. 0.207 gram salt titrated with permanganate, required 20.6 c.c. = 0.01648 gram. oxygen, corresponding to 7.96 per cent. |
| | II. 0.207 gram salt required 20.5 c.c. permanganate = 0.0164 gram oxygen, corresponding to 7.92 per cent. |
| | III. 0.302 gram salt required 29.9 c.c. permanganate = 0.02392 gram oxygen, corresponding to 7.92 per cent. |
| 2nd preparation. | IV. 0.302 gram salt, ignited and dissolved in acetic acid, required for precipitation of the uranium 7.8 c.c. of sodium phosphate solution = 7.8×0.01858 gram UO_3 = 0.145 gram UO_3 , corresponding to 47.99 per cent., or 39.99 per cent. of uranium. |
| | V. 0.2 gram salt after two days' exposure to the air, decolorised 19.7 c.c. permanganate = 0.01576 oxygen, corresponding to 7.88 per cent. |
| 3rd preparation. | VI. 0.2 gram salt, ignited in a covered porcelain crucible, lost 0.0498 gram, amounting to 24.9 per cent. |
| | VII. 0.35 gram salt ignited lost 0.087 gram, corresponding to 24.86 per cent. |
| | Experiments VI and VII were made from the same portion of slightly decomposed salt as Experiment V, and the residue after ignition in each case effervesced on addition of acetic acid. |
| | VIII. 0.2 gram ignited dissolved in dilute hydrochloric acid; the uranium precipitated by ammonium hydrate: the filtrate evaporated, and the residue ignited, weighed 0.0785 gram consisting of sodium chloride, equivalent to 0.0416 gram sodium oxide, or 20.8 per cent. |
| | The purity of this residue was ascertained by titration with decinormal silver nitrate solution, of which it required 13.2 c.c. This is equivalent to 13.2×0.0031 gram Na_2O = 0.0409 gram Na_2O or 20.45 per cent. |
| 4th preparation. | IX. The residue from Experiment VII dissolved in nitric acid, and the uranium precipitated by ammonia, gave after ignition 0.163 gram U_3O_8 , corresponding to 47.45 per cent. UO_3 , or 39.54 per cent. uranium. |
| | X. 0.9565 decomposed, dissolved in hydrochloric acid and precipitated by ammonia, gave 0.45 gram U_3O_8 , corresponding to 47.93 per cent. UO_3 , or 39.94 per cent. of uranium. |

XI. 0.2039 gram heated in a current of carbon dioxide gave 0.049 gram water and 11.1 c.c. of oxygen gas reduced to standard temperature and pressure. This corresponds to water 24.03 per cent. and oxygen 7.8 per cent.

These results agree with the formula $\text{UO}_6 \cdot 2\text{Na}_2\text{O} \cdot 0.8\text{H}_2\text{O}$ or $\text{UO}_3\text{Na}_4 \cdot 8\text{H}_2\text{O}$, as the following comparisons show :—

Calculated.			Found.					
			I. IV. VIII.	II. VII. IX.	III. X.	XI.	Mean.	
U	240	39.74	} 47.68	47.99	47.45	47.93	—	47.79
O ₃	48	7.94						
O ₃	48	7.95		7.96	7.92	7.92	7.8	7.90
2Na ₂ O ..	124	20.53		20.45	—	—	—	20.45
8H ₂ O....	144	23.84 (Difference 23.60)			—	—	24.03	23.81
	604	100.00		100.00				99.95

Red Sodium Peruranate, $\text{U}_2\text{O}_5 \cdot \text{Na}_2\text{O} \cdot 0.6\text{H}_2\text{O} = \text{UO}_6 \cdot \text{UO}_3 \cdot \text{Na}_2\text{O} \cdot 0.6\text{H}_2\text{O}$
(on the peroxide view $2\text{UO}_4 \cdot \text{Na}_2\text{O}_2 \cdot 0.6\text{H}_2\text{O}$).

This salt is precipitated before the preceding when a minimum quantity of sodium hydrate solution is used. On addition of alcohol it often separates out as a deep red oil, slowly becoming crystalline.

The following analyses have been made :—

- I. 0.85 gram salt gave 0.619 UO_3 , corresponding to 72.82 per cent. UO_3 or 60.68 per cent. uranium.
- II. 0.85 gram salt decolorised 65 c.c. permanganate = 0.052 gram oxygen, corresponding to 6.11 per cent.
- III. 0.85 gram salt gave 0.125 NaCl , equivalent to 0.0662 Na_2O , or 7.78 per cent.
- IV. 0.918 gram salt decomposed by heat and titrated with sodium phosphate solution, after dissolving the residue in acetic acid, required 36 c.c. = $36 \times 0.01858 \text{ UO}_3 = 0.6689 \text{ UO}_3$, corresponding to 72.86 per cent. UO_3 , or 60.72 per cent. uranium.

These results agree with the above formula, thus :—

		Calculated.	Found.			
			I.	II.	III.	IV.
U ₂	480	60.45	} 72.54		72.82	72.86
O ₆	96	12.09				
O ₃	48	6.05			6.11	
Na ₂ O	62	7.81			7.78	
6H ₂ O ...	108	13.60	(Difference.. 13.29)			
	<hr/> 794	<hr/> 100.00				

The ratio of the weights in this salt of the peroxide oxygen and of the uranium is 1 : 10 as in the case of the ammonium salt.

Potassium Peruranate,, $\text{UO}_6 \cdot 2\text{K}_2\text{O} \cdot 10\text{H}_2\text{O}$.

(*Double peroxide of uranium and potassium*, $\text{UO}_4 \cdot \text{K}_4\text{O}_4 \cdot 10\text{H}_2\text{O}$.)

This salt is obtained by adding alcohol to its solution prepared by treating uranic nitrate with potassium hydrate and hydrogen dioxide in excess. It separates as a yellow or orange precipitate, which is much more unstable than the corresponding sodium and ammonium compounds, rapidly absorbing carbon dioxide when exposed to the air, and losing oxygen. It is also readily decomposed by heat, giving off water and oxygen.

Both the analyses and the formation of the salt show that it contains three atoms of peroxide oxygen to one of uranium.

The following experiments may be quoted :—

25 c.c. of uranic nitrate solution containing 0.387 gram of uranium treated with 10 c.c. of hydrogen dioxide (3.23 per cent.) and potassium hydrate (10 per cent.) gave, on addition of 25 c.c. of alcohol (80 per cent.), a crystalline precipitate which slowly separated out of the liquid. The salt must be separated as rapidly as possible from the liquid to prevent decomposition and loss of oxygen.

The following experiment, made before the analysis of the salt, is instructive as showing the proportion of peroxide oxygen required for its formation.

78 c.c. of uranic nitrate solution containing 1.2 gram of uranium were mixed with excess of pure potassium hydrate solution, — 10 c.c. of a 20 per cent. solution. Hydrogen dioxide was then slowly run in from a burette into the liquid, which was thoroughly shaken after each addition of the dioxide. It was found that to effect complete solution of the uranic hydrate in the alkaline liquid 12 c.c. were required containing 0.24 gram of peroxide oxygen. One atom or 240 parts of uranium would, therefore, require three atoms or 48 parts of

oxygen from the hydrogen dioxide* to produce the new soluble compound.

Owing to partial decomposition, I have been compelled to reject a large number of analyses made of this salt. The following were made the same day that the salt was prepared:—

- I. 0.71 gram decolorised 60 c.c. permanganate = 0.048 gram oxygen, corresponding to 6.76 per cent.

The same, after being reduced by treatment with zinc and sulphuric acid, required 20.5 c.c. permanganate equivalent to 0.295 gram UO_3 , or 41.55 per cent. UO_3 , or 34.61 per cent. uranium.

- II. 0.126 gram decolorised 10.8 c.c. permanganate = 0.00864 gram oxygen, corresponding to 6.87 per cent.

The same after reduction required 3.6 c.c. permanganate, equivalent to 0.05184 gram UO_3 , or 41.14 per cent., or 34.18 per cent. of uranium.

- III. 0.13 gram decolorised 11 c.c. permanganate = 0.0088 gram oxygen, corresponding to 6.77 per cent.

These results agree with the above formula, thus:—

			Found.				
			I.	II.	III.	Mean.	
U	240	$\left. \begin{array}{l} 34.07 \\ 6.81 \end{array} \right\} \text{UO}_3$ 40.88	41.55	41.14	—	41.29
O ₃	48					
O ₃	48		6.76	6.87	6.77	6.80
2K ₂ O	188.4	26.75				
10H ₂ O	..	180	25.56				
		<hr/>					
		704.4	100.00				

The water in this formula is given only as that agreeing with the percentage composition of the salt dried by pressure between folds of filter paper.

IX. ON HIGHER OXIDES OF TUNGSTEN AND MOLYBDENUM. (Preliminary Notice.)

Tungstic dihydrate dissolves readily in solution of hydrogen dioxide, even in presence of much free acid, forming a liquid comparatively stable in dilute solutions, but which, in the case of strong acid solutions, gradually deposits insoluble tungstic oxide.

* 1 c.c. of this dioxide titrated at the same time required 25 c.c. permanganate solution, and contained therefore .02 gram oxygen. An experiment, with similar result, was made with sodium hydrate.

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IV.—*The Alkaloids of the Aconites. Part I. On the Crystallisable Alkaloids contained in Aconitum Napellus.*

By C. R. ALDER WRIGHT, D.Sc., Lond., Lecturer on Chemistry in St. Mary's Hospital Medical School.

IN a preliminary notice read before the Chemical Society in 1875 and printed amongst the abstracts in the *Chem. Soc. Journal* [2], xiii, 1265, the author and Mr. G. H. Beckett described the first results obtained from the examination of various products extracted by Mr. T. B. Groves (Weymouth), from *Aconitum ferox* and *A. Napellus*, the mode of extraction adopted being percolation of the ground dry roots with alcohol slightly acidulated with hydrochloric acid, evaporation to a small bulk of the extract thus obtained, precipitation of bases by ammonia, and extraction by ether of the alkaloids thus precipitated. In this way there was isolated from the *A. ferox* an alkaloid crystallisable from ether, but yielding salts that wholly refused to crystallise, drying up to varnishes readily soluble in water: apparently this substance is the main ingredient in the preparations which have been designated by various chemists "English aconitine," "pseudoaconitine," "acraconitine," &c. On analysis, this body gave numbers represented by the formula $C_{38}H_{49}NO_{11}$, the gold salt being $C_{38}H_{49}NO_{11} \cdot HCl \cdot AuCl_3$. Further experiments on the "constitution"

of this substance are in progress, and will be described in a subsequent memoir.

Very different results, however, were obtained with *A. Napellus*. Few substances of high physiological activity have formed the subject of examination by more chemists and pharmacists than this body; and with few, if any, have more contradictory results been obtained: this want of uniformity in results appears to arise from many causes. In the first place, it seems excessively probable that due care in selecting the roots examined was not always exercised, so that the roots of different species were probably mixed together: there seems, from the results obtained by Mr. Groves and the author, some reason for supposing that entirely different bases are obtainable from different species. In the next place, the mode of extraction employed was, in most instances, such as must inevitably have caused a large amount of alteration and decomposition of the alkaloids present during the process of extraction, the alcoholic extracts having generally been heated in contact either with a mineral acid or with an alkali, or both; as the active principle of aconite roots is known to be of a highly unstable character, the chances of uniform results being obtained by such processes are very small. Lastly, with only one or two exceptions, the substances isolated have not been subjected to analysis, and absolutely no numerical results have been given by the majority of writers and experimenters.

Thus, the only numerical values that the author has been able to find recorded prior to 1870 are those of von Planta (*Annalen der Chemie*, lxxiv, 257): and that the substance examined by this chemist did not present satisfactory indications of purity, and indeed of authenticity, is manifest from the circumstance that the material examined was purchased from Merck, who had not prepared it himself, and that it was an amorphous powder. No history of its preparation from the root is given, but presumably it was extracted by the process of Geiger and Hesse, who first discovered the alkaloidal character of the active principle of *A. Napellus* roots; this process involves heating the alkaloid in contact first with lime, and secondly with sulphuric acid, which could hardly fail to bring about considerable alteration in so unstable a body as the active principle is known to be. For these reasons, therefore, the formula arrived at by von Planta, viz., $C_{20}H_{41}NO_7$, the hydrochloride being $C_{20}H_{41}NO_7 \cdot 2HCl$ (!) must be regarded as open to grave objection (*vide infra*).

In 1860, Mr. Groves succeeded in isolating from *A. Napellus* a crystalline alkaloid possessing high physiological activity and forming well crystallised salts (*Pharm. J. Trans.* [2], viii, 121); this was exhibited in the Exhibition of 1862 (as was also a specimen of a crystallised alkaloid obtained by Morson, but which was apparently not

derived from *A. Napellus*). Unfortunately, Mr. Groves' product was not analysed at the time, but a portion of the nitrate of the sample thus obtained has subsequently been examined by the author and Mr. Beckett: the crystals of base regenerated from the nitrate by ammonia and ether, gave the following values:—

0.2270 gram gave 0.5235 CO_2 and 0.1480 H_2O .
 0.2975 " " 0.6845 " " 0.1955 "
 0.5795 " of gold salt gave 0.1200 Au.

	Calculated for $\text{C}_{32}\text{H}_{48}\text{NO}_{10}$.	Calculated for $\text{C}_{32}\text{H}_{48}\text{NO}_{11}$.	Found.	
Carbon in free base . . .	63.89	62.34	62.90	62.75
Hydrogen	7.15	6.97	7.24	7.30
Gold in gold salt	20.85	20.50	20.71	

From the results detailed below, the conclusion is unavoidable that this product either was imperfectly purified, or else had been somewhat altered and diminished in molecular weight during its extraction; the latter is not at all improbable, as the specimen had been purified by conversion into the insoluble mercuric iodide compound, and regeneration from this substance. The author has found, in the case of the base derived from *A. ferox*, above alluded to, that the mercuric iodide process actually does cause a considerable amount of change of this character.

Some years subsequently (1871 and 1872) M. Duquesnel succeeded in isolating from *Aconitum napellus* a well-crystallised base to which he gave the name "aconitine cristallisée," to distinguish it from the amorphous preparations met with in commerce under the name of aconitine. The process employed was extraction with alcohol acidulated with tartaric acid, evaporation of the extract at temperatures not exceeding 60° , precipitation by sodium bicarbonate, and crystallisation of the precipitate from a mixture of ether and light petroleum spirit (*Compt. rend.*, lxxiii, 207; also *Ann. Chim. Phys.* [4], 25, 151). M. Duquesnel gave the following numbers as obtained from this preparation:—

Carbon	59.96	60.18
Hydrogen	7.35	7.54
Nitrogen	2.58	2.69

from which he deduced the formula $\text{C}_{27}\text{H}_{46}\text{NO}_{10}$. The experiments described below clearly show that this product could not have been pure, inasmuch as frequently repeated crystallisation does not suffice to separate completely the crystallisable alkaloid contained in *A. Napellus* from another amorphous substance of lower molecular weight obtained along with it by M. Duquesnel's process.

In 1874, wishing to obtain a larger supply of the crystalline base from *A. Napellus* isolated by him in 1860, Mr. Groves operated on two batches of 1 cwt. each of roots purchased as *Aconitum Napellus*, and presenting the appearance of that species; whether, however, there was not a large admixture of some other species, or whether the roots examined were of abnormal character from some peculiarity of soil or climate, is open to question, from the totally unexpected nature of results obtained with these roots. On working up the extract obtained by means of alcohol acidulated with hydrochloric acid, a well-crystallised mass was obtained consisting of the mixed nitrates of two entirely dissimilar bases (*Year-book of Pharmacy*, 1874, 507). Of these one, when in the free state, crystallised readily from ether, and has been found by the writer to be identical with the alkaloid obtained in an imperfectly pure condition by M. Duquesnel; the other wholly refused to crystallise from ether or any other solvent when in the free state, although the varnish-like products obtained on evaporation of the solutions of the base readily formed well-crystallised salts on moistening with dilute mineral acids. Curiously enough, whilst the former base was highly active physiologically, the latter was almost inert, half-grain doses being taken internally by Mr. Groves without the production of any marked symptoms. It seems not at all improbable that the very varying activity exhibited by different commercial preparations sold as "aconitine" may be at least partly due to the circumstance that the usual modes of preparation of the drug are not calculated to effect any separation of the active alkaloid from the inert base, should the latter be contained in the roots employed.

These products obtained by Mr. Groves have been subjected to careful examination by the author with the following results:—

A. Comparatively inert Base. Picraconitine.—The salts of the comparatively inert base when tasted do not produce the peculiar prickling of the tongue characteristic of aconite roots, but simply have a bitter taste; for which reason it is suggested that the term "picraconitine" may be conveniently employed to designate this base. It was at first thought by Mr. Groves that this substance might be identical with the body isolated by Broughton from *Aconitum heterophyllum* (called atees in India) and termed by him *atisine*, but the numerical values obtained and other circumstances are quite inconsistent with the identity of the two bodies. Thus Broughton found (*Medical Press and Circular*, May 27, 1874) that *atisine* melted at 85°, formed crystalline salts only with difficulty, and gave a platinum salt pretty readily; from this last the formula $C_{16}H_{24}N_2O_8$ was deduced; picraconitine, on the other hand, does not fuse at 100°, forms crystalline salts with great ease, forms a platinum salt so soluble in water that it is only precipitated in very concentrated solutions, and cannot be

washed without almost wholly dissolving; and, lastly, yields numbers leading to the formula $C_{31}H_{45}NO_{10}$.

(1) Crystals of picraconitine hydrochloride prepared by Mr. Groves (*loc. cit.*) and purified by several recrystallisations, 0.6190 gram (air-dry) lost at 100° 0.0295 gram.

(2) Ditto, recrystallised from water, 0.4725 gram (air-dry) lost at 100° 0.0280 gram.

(3) Ditto, again recrystallised from water, 0.5260 gram (air-dry) lost at 100° 0.0190 gram.

(4) Ditto, yet again recrystallised from water, 0.9190 gram (air-dry) lost at 100° 0.0380 gram.

Calculated for $C_{31}H_{45}NO_{10}, HCl, 1\frac{1}{2}H_2O$.	Found.			
	(1.)	(2.)	(3.)	(4.)
4.13	4.77	4.87	3.61	4.13

Specimen (1) 0.2680 gram, dried at 100° , gave 0.5755 CO_2 and 0.1850 H_2O .

Specimen (1) 0.4490 gram, dried at 100° , gave 0.1000 AgCl.

Specimen (4) 0.3520 gram, dried at 100° , gave 0.7555 CO_2 and 0.2400 H_2O .

Specimen (4) 0.3320 gram, dried at 100° , gave 0.0750 AgCl.

„ „ 0.5050 „ „ „ „ 0.1100 „

„ „ 0.4790, burnt with soda lime, gave 0.0735 Pt.

	Calculated.		Found.		
	(1.)	(2.)	(1.)	(4.)	
C_{31}	372	59.29	58.56	58.53	
H_{45}	46	7.33	7.67	7.58	
N.....	14	2.23	—	2.18	
O_{10}	160	25.49	—	—	
Cl	35.5	5.66	5.51	5.59	5.44

$C_{31}H_{45}NO_{10}, HCl$. . 627.5 100.00

Picraconitine, precipitated from hydrochloride No. 4 dissolved in ether and obtained as a varnish by spontaneous evaporation, not fusible at 100° . 0.2460 gram gave 0.5675 CO_2 and 0.1745 H_2O .

	Calculated.		Found.	
	(1.)	(2.)	(1.)	(2.)
C_{31}	372	62.95	62.91	
H_{45}	45	7.61	7.88	
N.....	14	2.37		
O_{10}	160	27.07		
$C_{31}H_{45}NO_{10}$	591	100.00		

Picraconitine aurochloride is precipitated in canary-yellow flakes not

perceptibly crystalline and exceedingly sparingly soluble in water on addition of gold chloride to picroaconitine hydrochloride solution. After drying over sulphuric acid it does not alter at 100°.

From hydrochloride (1) 0.6790 gram gave 0.1430 Au = 21.06 per cent.

" " (2) 0.6995 " " 0.1475 " 21.09 "

1.1170 " " 0.2380 " 21.35 "

Average..... 21.15

Calculated for $C_{21}H_{45}NO_{10}, HCl, AuCl_3$ 21.07

It is noteworthy that no indications of the presence of this base were observed by Mr. Groves in his former experiments (1860), nor was any such body obtained in the author's experiments described below; the circumstance, however, that roots purchased as *Aconitum Napellus* were found on this one occasion to yield a crystallised product (nitrate), of which by far the larger proportion was a substance inert as compared with the active principle of the roots, is of great pharmaceutical importance, as tending to throw light on the great discrepancies sometimes noticed in the physiological potency of different specimens of the drug met with in commerce under the name of "aconitine."

B. Physiologically active Base. Aconitine—The base, crystallisable from ether and possessing high physiological activity, was separated by the author from the mixture of nitrates of this alkaloïd and of picroaconitine obtained by Mr. Groves (*loc. cit*) by simply dissolving in ether the mixture of bases precipitated from the mixed nitrates by ammonia and leaving the solution to evaporate spontaneously; in this way a small quantity of crystals was obtained which, after two recrystallisations from ether, gave the following numbers:—

Carbon in free base 62.90

Hydrogen 7.45

Gold in gold salt 20.32

These numbers agree fairly with those required for the formula $C_{23}H_{45}NO_{11}$, and are almost identical with those obtained from the crystallised base isolated by Mr. Groves in 1860 (*supra*). The two products agreed closely in all their characters, and, moreover, they exactly agreed with M. Duquesnel's description of his "aconitine cristallisée." The experiments which follow clearly demonstrate that each one of these three bodies must have consisted essentially of the same alkaloïd, but not in a state of purity; when pure, this base (to which it is proposed to restrict the term *aconitine* for scientific purposes) is indicated by the formula $C_{23}H_{45}NO_{11}$.

The imperfectly purified crystalline base obtained from the mixed nitrates as above described did not materially alter in molecular weight by recrystallisation and appeared to be uniform in character; but on dissolving it in slightly warm dilute hydrochloric (or better hydrobromic acid) and allowing the solution to crystallise, a salt was produced from which a base was regenerated by sodium carbonate and ether, apparently identical with the original substance, but giving somewhat different numbers. On repetition of the process no further change in the base was produced, whence it is evident that aconitine (like certain other alkaloids, *e.g.*, papaverine) has so strong a tendency to adhere to other substances found along with it, that simple crystallisation of the free base several times successively is insufficient to purify it completely, although conversion into a crystallisable salt and recrystallisation of the latter effects a complete separation. The following numbers were obtained with the pure base thus regenerated from the hydrobromide:—

0.2245 gram gave 0.5080 CO₂ and 0.1370 H₂O.

	Calculated.		Found.
C ₃₃	396	61.39	61.71
H ₄₃	43	6.67	6.78
N.....	14	2.17	
O ₁₃	192	29.77	
<hr/>			
C ₃₃ H ₄₃ NO ₁₃	645	100.00	

After solution in warm dilute hydrochloric acid, crystals of the hydrochloride were formed; of these, when air-dry,

0.5140 gram lost at 100° 0.0390 gram = 7.59 per cent.

The formula C₃₃H₄₃NO₁₃, HCl, 3H₂O requires 7.34 ..

0.4750 gram of dry salt gave 0.0995 AgCl .. Cl = 5.18 ..

Calculated for C₃₃H₄₃NO₁₃, HCl..... Cl = 5.21 ..

The hydrobromide, recrystallised from water, gave the following values:—

0.4087 gram (air-dry) lost at 100° 0.0250 = 6.11 per cent.

Calculated for C₃₃H₄₃NO₁₃, HBr, 2½H₂O.. = 5.83 ..

0.3837 gram of dry salt gave 0.1000 AgBr.. Br = 11.09 ..

Calculated for C₃₃H₄₃NO₁₃, HBr = 11.02 ..

On addition of auric chloride to the aqueous solution of this hydrochloride, pale-yellow amorphous flakes of a gold salt, very sparingly soluble in water, were thrown down; after complete drying over sulphuric acid in the dark, these lost no weight at 100°; in a thin film,

however, the salt slightly darkened in the light in the course of a day or two at the ordinary temperature.

0.4630 gram of gold salt dried at 100° gave 0.0925 Au
gold = 19.98 per cent.

Calculated for $C_{33}H_{43}NO_{12}, HCl, AuCl_3$ = 19.92 „

These numbers clearly show that pure aconitine, when regenerated from a crystallised pure salt, is expressed by the formula $C_{33}H_{43}NO_{12}$: the difficulty in obtaining the base pure by simply recrystallising it from ether is exactly that which is noticed in the case of *papaverine*, which, as was first pointed out by Hesse and subsequently by the author and Mr. Beckett (this Journal, May, 1876), cannot be obtained pure by simple recrystallisation, but is readily purified by converting the approximately pure substance into a crystallisable salt (acid oxalate), recrystallising this, and regenerating the alkaloid from the product.

With the object of submitting aconitine to a thorough chemical investigation, 2 cwts. of *Aconitum Napellus* roots were worked up by Messrs. Hopkins and Williams to a condensed extract in accordance with the directions of M. Duquesnel, this “tartaric acid process” being employed rather than one involving the use of a mineral acid, in order to avoid possible decomposition: it seems by no means improbable that the amorphous and ill-defined substances described by Hübschmann and others under the name of napelline, acolyctine, lycoctonine, &c., may be really only aconitine or some allied body more or less altered and decomposed during the extraction process. The ground root was percolated by alcohol acidulated with tartaric acid (about 60 gallons of alcohol and 1 lb. of tartaric acid being employed altogether), and the extract was evaporated to a small bulk at as low a temperature as possible. About 5 gallons of condensed extract were then obtained, which was worked up by the author as follows:—The liquid, consisting of a clear brown-red aqueous portion and a dark soft resin, was exposed to the air in shallow vessels for a few days to dissipate some of the remaining alcohol, and was then diluted with water and filtered from resin; the aqueous filtrate was agitated with benzoline (light petroleum distillate) whereby some remaining resin was removed, and the aqueous liquid was then precipitated by a slight excess of potassium carbonate: the filtrate contained a base soluble in carbonate of potassium, which gave a copious precipitate with mercuric iodide dissolved in potassium iodide: this precipitate when decomposed by sulphuretted hydrogen, finally yielded a small quantity of crystals of aconitine, but chiefly consisted of a base which appeared to be wholly non-crystalline and to form non-crystalline salts, and much resembling (if, indeed, not identical with)

the non-crystalline base or mixture of bases obtained, as described below, from the mother-liquors left on recrystallising the potassium carbonate precipitate.

The precipitate thrown down by the potassium carbonate was agitated with ether, and the ethereal solution thus obtained with tartaric acid solution; the ether thus freed from base was used over again several times: finally the whole of the precipitate was thus dissolved with the exception of some humus-like flakes: the ether left after agitation with tartaric acid contained in solution a small quantity of a clear soft yellow resin. The acid tartrate solution thus obtained was systematically worked up, in order to discover if more than one crystalline alkaloid was present; it was first precipitated with sodium carbonate, and the precipitate agitated with successive small quantities of ether, whereby finally a considerable portion was left undissolved in the form of snow-white crystalline flakes: the ethereal solution thus obtained gave by spontaneous evaporation a copious crop of slightly coloured crystals, which were filter-pumped, dissolved in benzene, and precipitated by addition of benzoline (light petroleum spirit): finally, the mother-liquors and drainings of these crystals were evaporated and the residue dissolved in dilute acetic acid, whereby a little resin was left undissolved: the solution was treated with a little sodium carbonate to throw down colouring matter and remaining resin, and the filtrate with excess of sodium carbonate and ether; this ethereal solution gave successive crops of crystals on spontaneous evaporation with a final syrupy mother-liquor, which dried up to a varnish and refused to yield any crystalline salts on solution in acids and spontaneous evaporation: it could not therefore have contained any considerable amount of picraconitine: this final product gave the following numbers:—

Carbon in base	66.39
Hydrogen	7.94
Gold in gold salt	23.91

which are not far removed from the numbers found by von Planta (*loc. cit. supra*), and from which he deduced the formula $C_{20}H_{27}NO_7$, viz.:—

				Another sample.	
Carbon in free base ..	67.81	68.34	67.75	64.83	66.95
Hydrogen	8.82	8.90	8.64	8.14	8.59
Nitrogen	—	3.59	3.31	—	—
Gold in gold salt	—	22.06	—	—	—

It can, therefore, hardly be doubted that the product examined by von Planta consisted mainly of the non-crystalline base (or mixture

of decomposition-products formed during extraction?) just described. It may be noticed that von Planta's numbers represent the gold salt as being $C_{30}H_{47}NO_7 \cdot HCl \cdot AuCl_3 + H_2O$ (?), whilst what he regarded as a hydrochloride, $C_{30}H_{47}NO_7 \cdot 2HCl$, must evidently have been formed by an action of the hydrochloric acid different from mere combination.

In this way three batches were obtained:—

(A.) Left undissolved by ether at first (ether not employed in large quantity).

(B.) Crystals deposited from first ethereal solution and purified by benzene and petroleum.

(C.) Crystals from mother-liquors.

Each one of these batches, when fractionally crystallised from ether, yielded the same numbers, in all cases closely approximating to those required for the formula $C_{33}H_{43}NO_{12}$, but giving a gold salt containing a little too much gold; when, however, these approximately pure specimens were converted into hydrobromides, and the drained and washed crystals of that salt were treated with sodium carbonate and ether, crystals of base were obtained perfectly corresponding with the substance similarly purified from Mr. Groves' products described above and designated *aconitine*, and giving exactly the numbers required for the above formula. Thus the following numbers were obtained with the substance purified only by crystallisation from ether:—

Specimen No. 1. Crystals left undissolved by ether (A) converted into gold salt—

0.8045 gram gave 0.1640 Au.

0.9210 " " 0.1875 "

No. 2. (A) treated with ether sufficient to dissolve one-third; solution crystallised by spontaneous evaporation—

0.2615 gram gave 0.5840 CO_2 and 0.1600 H_2O .

0.4825 gram gold salt gave 0.0980 Au.

No. 3. Portion of (2) insoluble in ether similarly treated: crystals from this second ethereal fractional solution—

0.3545 gram gave 0.7880 CO_2 and 0.2200 H_2O .

0.2720 " " 0.6060 " 0.1670 "

0.5730 " gold salt gave 0.1165 Au.

No. 4. Crystals left undissolved from (3)—

0.2830 gram gave 0.6380 CO_2 and 0.1730 H_2O .

0.2880 " " 0.6475 CO_2 and 0.1800 H_2O .

0.6760 " gold salt gave 0.1375 Au.

No. 5. (B) recrystallised from ether—

0.2700 gram gave 0.5980 CO₂ and 0.1620 H₂O.

0.5630 „ gold salt gave 0.1140 Au.

No. 6. (C) recrystallised from ether—

0.2525 gram gave 0.5705 CO₂ and 0.1520 H₂O.

0.5615 „ gold salt gave 0.1135 Au.

0.5190 „ „ „ 0.1050 „

	Carbon in base.	Hydrogen in base.	Gold in gold salt.
No. (1)	—	—	20.38
„	—	—	20.36
(2)	60.91	6.79	20.31
(3)	60.62	6.89	20.33
„	60.76	6.82	—
(4)	61.48	6.79	20.34
„	61.32	6.94	—
(5)	60.40	6.67	20.25
(6)	61.62	6.69	20.23
	—	—	20.21
Average	61.02	6.79	20.30
Calculated for C ₃₃ H ₄₅ NO ₁₂	61.39	6.67	19.92

Specimens Nos. 2, 3 and 4 (A) were mixed and converted into hydrobromides, as was No. 5 (B) and also No. 6 (C). The recrystallised salts gave the following numbers:—

Purified hydrobromide I (from A) 0.3850 gram of air-dry salt lost at 100° 0.0230 = 5.97 per cent.

Purified hydrobromide II (from B) 1.3800 gram of air-dry salt lost at 100° 0.0820 = 5.94 per cent.

Calculated for C₃₃H₄₅NO₁₂, HBr, 2½H₂O = 5.83 per cent.

I. 0.3620 gram dried at 100° gave 0.0945 AgBr Br = 11.11 p. c.

II. 0.5720 „ „ „ „ 0.1485 „ „ 11.05 „

Calculated for C₃₃H₄₅NO₁₂, HBr = 11.02 „

The base regenerated from these three specimens gave these values—

Base from hydrobromide I.—0.2660 gram gave 0.5955 CO₂ and 0.1600 H₂O.

„ II.—0.2440 „ 0.5500 CO₂ and 0.1520 H₂O.

„ III.—0.3005 „ 0.6800 CO₂ and 0.1850 H₂O.

	Calculated.		Found.			Mean.
	I.	II.	III.			
C ₃₃	396	61·39	61·06	61·47	61·71	61·41
H ₄₃	43	6·67	6·68	6·92	6·84	6·81
N	14	2·17	—	—	—	—
O ₁₂	192	29·77	—	—	—	—
<hr/>						
C ₃₃ H ₄₃ NO ₁₂ ..	645	100·00				

The gold salts gave these values :—

From I.	0·8445	gram	gave	0·1690	Au	=	20·01	per cent.
„ II.	0·5725	„	„	0·1145	„	=	20·00	„
„ III.	0·6210	„	„	0·1240	„	=	19·97	„

Average 19·99 „

Calculated for C₃₃H₄₃NO₁₂,HCl,AuCl₃ = 19·92 „

From these numbers it is clear that the *Aconitum Napellus* roots examined contained only one base crystallisable from ether; and that this base, when perfectly pure, was identical with the *aconitine*, C₃₃H₄₃NO₁₂, previously isolated in an approximately pure crystallised state by Groves, and subsequently by Duquesnel, the different formula arrived at by the latter being due to the imperfect purity of the alkaloid extracted by him.

The quantity of crystallised base, C₃₃H₄₃NO₁₂, isolated from the 2 cwts. of roots amounted to a little upwards of an ounce, the total amount of alkaloids (amorphous products included) being some 2½ ozs.; this represents a yield of about 0·03 per cent. of crystallised base, and 0·07 per cent. of total bases. M. Duquesnel states that the amount of “aconitine crystallisée” obtainable from *A. Napellus* varies from 0·6 gram, and even none at all, to 4 grams per kilo., *i.e.*, from 0·06 to 0·40 per cent. It may be noticed in this connection that the values given by Proctor, Zinoffski and others, as to the amount of alkaloid present in aconite roots simply represent the total alkaloids, crystalline and non-crystalline, and give no clue as to how much of either kind was present; inasmuch, however, as these values differ with the country in which the roots were grown, &c., &c., it is extremely probable that the amount of crystalline base, C₃₃H₄₃NO₁₂, will be found to vary according to circumstances.

It is proposed to study the chemical relationships and the “constitution” of this alkaloid, and the allied bases from *A. ferox* (pseudocointine, C₃₃H₄₃NO₁₁). The physiological action of aconitine is excessively energetic, so much so as to render working with it a matter of considerable pain and difficulty, unless great care be taken in manipulation, and more especially in avoiding the inhaling of the dust of the

crystals of the base or its salts. A minute fragment, too small to be seen, if accidentally blown into the eye, sets up the most painful irritation and lachrymation, lasting for hours; whilst similar particles, if inhaled, produce great bronchial irritation or profuse sneezing, and considerable catarrh or "sore throat," according to the part where they lodge.

The following sentences summarise the results obtained as above described from the work of Mr. Groves and the author.

1. *Aconitum Napellus* roots, as met with in commerce, yield by appropriate means a highly active, well-crystallised alkaloid (*aconitine*), which is represented by the formula, $C_{33}H_{43}NO_{12}$; the crystallised bodies obtained formerly by Groves (1860), and by Duquesnel (1871), consisted mainly of this base, but were not perfectly pure.

2. It has happened in one instance that roots purchased as *A. Napellus* yielded only a small quantity of aconitine, and that a large amount of a nearly inert bitter base, yielding well crystallised salts (*picraconitine*) was also present. The preparations usually met with in pharmacy under the name of "aconitine," or "nitrate of aconitine," must necessarily contain this inert base whenever it was present in the roots employed; and consequently such pharmaceutical preparations cannot be relied on as of uniform physiological potency.

3. Besides *aconitine* and *picraconitine*, *A. Napellus* roots contain another alkaloid (alteration product of aconitine produced during extraction?) of lower molecular weight, and incapable of yielding crystalline salts or of crystallising itself. Commercial "aconitine," when not crystallised, is liable to contain this substance as an impurity; thus the body examined by von Planta appears to have almost wholly consisted of this amorphous, uncrystallisable substance, which is perhaps identical with or may contain the body "napelline," and other analogous substances described by other chemists.

4. The physiologically active crystallisable alkaloid of *A. Napellus* (*aconitine*) appears to be wholly dissimilar from the crystallisable alkaloid of *A. ferox* (*pseudoaconitine*), although the two are doubtless allied, and are similar in many of their properties. The inactive bitter base of *A. Napellus* (*picraconitine*) is not identical with Broughton's atisine from *A. heterophyllum*.

5. The use of strong mineral acids and other reagents in the extraction of aconite alkaloids from the roots (as in the older processes of Geiger and Hesse, of Hottot and Liégeois, &c.), is extremely likely to cause loss of crystallisable aconitine by alteration and decomposition; and to this cause is to be attributed the statement of chemists who have used such processes, that the alkaloid of *A. Napellus* is non-crystalline. Not improbably the "lycoctinine" and "acolyctine" of Hülschmann, from *A. lycoctonum*, are alteration-products thus

formed. The tartaric acid process of M. Duquesnel is preferable, but in view of the first rough crystals of base thus produced being impure, and of the difficulty of separating a mixture of the crystallised salts of aconitine and picroaconitine, it is desirable that in future the substance employed medicinally should have been prepared and separated from picroaconitine (if present) by extracting the mixed alkaloids from the roots by Duquesnel's process; recrystallising the crude aconitine crystals thus obtained from ether or analogous solvents, so as to separate picroaconitine and the other non-crystalline bodies; converting into a crystallised salt (for which purpose the hydrobromide is well fitted); and finally regenerating the alkaloid (if required in the free state) by sodium carbonate, and crystallising from ether; in this way a perfectly definite homogeneous substance is obtained, possessing in a high degree the physiological powers of aconite root.

V.—Notes on some Experiments made with a view to ascertaining the Practical Nature of a Proposed Method of Determining the Mineral Strength of Soils by means of Water-culture.

By G. A. HIGHT, Indian Forest Department.

THE usual object of water-culture experiments is to ascertain what particular salts are congenial or necessary to the growth of any particular plant. When a plant is grown in an artificially prepared solution, so that it can obtain its nourishment solely from the salts contained in that solution, the exact effect of any salt upon the growth of the plant can be easily observed by adding that salt to, or abstracting it from, the solution. In order to ascertain whether any soil will sustain any plant, the usual plan is to examine chemically the soluble matter in the soil. If the soluble salts correspond to those which have been shown by water-culture, or by other means, to be suitable to the growth of the plant, then the soil is regarded as chemically capable of sustaining the plant.

The object of the experiments, the results of which are tabulated on page 159, was to combine these two processes. The plant was grown in a watery extract of the soil to be examined, and it was thought by observing its development and durations, to obtain a practical test of the suitability of the soil for the plant, in other words of the strength of the soil. If several soils were tested at one time, the results might,

it was believed, be referred to one another, or to a known artificial solution, and expressed in figures.

It must be borne in mind that nothing further was intended than to find a means for determining the *chemical* strength of the soil, and that the more important factors—more important at least from a forestal point of view—of moisture, situation, &c., are not taken into account.

In order that the experiments might be exhaustive, it would, properly speaking, be necessary to prepare the solutions with water containing carbonic acid, as it is well known that many of the nourishing salts (phosphates and carbonates), insoluble in pure water, are readily soluble in water containing carbonic acid. But as these experiments were only regarded as preliminary, to ascertain the practical value of the method, it was considered sufficient to use pure water. Solutions of some of the salts of the organic acids produced by the decay of vegetation also dissolve the phosphates and carbonates; but to introduce these into the solution would complicate matters unnecessarily, for it is only proposed to test the *mineral* strength of the soil.

The following soils were tested:—

A. Loam from Garko forest. This soil was selected from a spot where the trees were dying off.

B. Loamy sand from Helaya forest, taken from inside a large enclosure, where the young growth was doing very well.

C. Loamy sand from Kirsar forest.

D. Loam from Butta forest, selected from between two of the largest trees.

E. Clay from Ghaz forest, mountain soil; taken from a part of the forest where the trees were most dense.

All these soils, excepting E, were first deposited from the River Indus. D, B, and E were supposed, from the growth of the forest upon them, to be rich soils; A and C to be poor ones. It must, however, be remembered that the growth of the forest is no test for the *mineral* strength of the soil.

Each specimen was taken at a depth of $1\frac{1}{2}$ feet from the surface.

The proportion of the solutions was 1 ounce of soil to each pint of water.

The solutions were prepared as follows:—

4 ounces of very carefully dried and sifted soil were placed in a porcelain evaporating dish. One pint of distilled water was poured over it. The dish was placed in a sand-bath, and the contents slowly raised to a temperature of 212° Fah. They were then allowed to cool, and, after settling for a short time, as much as possible of the muddy water was poured off into a second vessel. Over the remaining soil, another pint of distilled water was poured; this raised to 212° Fah.,

and decanted as before. On the soil before it dried, a third pint of water was poured and decanted off, and similarly with a fourth. The decanted liquid was then twice filtered. There resulted 3 pints 6 ounces of solution. Distilled water was then added sufficient to bring the whole up to 4 pints. This just more than filled three wine bottles of very opaque glass.

All the soils were treated in this way in succession, and three bottles filled with the extract from each. They were then numbered, and labelled as follows:—

1 }		7 }		13 }	
2 }	Garko.	8 }	Kirsar.	14 }	Ghaz.
3 }		9 }		15 }	
4 }		10 }		16 }	Normal
5 }	Helaya.	11 }	Butta.	17 }	solution.
6 }		12 }			

No. 3 was damaged, owing to the bottle into which the extract was placed not having been properly cleaned.

Seedlings of "*Acacia arabica*" were placed in the solutions on July 25th, eight days after they had been sown. The seedlings were so selected as to be very nearly equal in development and in weight from amongst a very large number. The more vigorous ones were chosen, and great care was observed that they should be entirely free from any damage caused by removal from the soil, &c. The stage at which the seedlings had arrived was about as follows:—The cotyledons had just opened out; the peduncle was scarcely beginning to develop itself; the root was 2—3 inches in length, and the average weight of the plants, 0.32 grams. A notch was cut in the cork of each bottle, and the seedling was supported by a ball of cotton-wool in such a way that the surface of the solution was at exactly the same point where the surface of the soil had been before.

In Nos. 16 and 17, labelled "normal solution," was a solution prepared artificially by the recipe given in Prof. Johnston's "*How Crops Grow*," p. 155. The solution gave a slightly acid reaction.

Every morning the portion of the solution taken up by the plants was replaced with distilled water, in order that the roots should always remain at the same depth in the water. Every other morning the plants were carefully taken out, dried on a piece of blotting paper, and weighed. The weights are noted in the appended register.

This was continued until August 20th, when the experimenter met with an accident, and the plants could no longer be attended to. Fresh distilled water was, however, poured in every morning; but they were no longer properly cared for, and three or four were destroyed by accident. The remainder, however, continued to flourish, and were all alive at the end of October, when some of them were about 8 inches high.

Date.	A. Loam from Gar-ko Forest, selected where the trees were dying off (August 2-4, solution alkaline).			B. Loamy sand from Hclyn Forest, taken where the young growth was doing very well.			C. Loamy sand from Kirsar Forest.			D. Loam from Butia Forest, from between two of the largest trees.			E. Clay from Glaz Forest, mountain soil; taken where the trees were the most dense.			Normal solution.	
	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 4.	Expt. 5.	Expt. 6.	Expt. 7.	Expt. 8.	Expt. 9.	Expt. 10.	Expt. 11.	Expt. 12.	Expt. 13.	Expt. 14.	Expt. 15.	Expt. 16.	Expt. 17.
July 26,	Grms. 0.37	Grms. 0.24	Grms. 0.36	Grms. 0.32	Grms. 0.27	Grms. 0.32	Grms. 0.34	Grms. 0.30	Grms. 0.33	Grms. 0.31	Grms. 0.29	Grms. 0.30	Grms. 0.28	Grms. 0.29	Grms. 0.28	Grms. 0.35	Grms. 0.28
" 27,	0.45	0.29	0.34	0.33	0.33	0.37	0.41	0.36	0.43	0.36	0.32	0.35	0.33	0.30	0.30	0.32	0.32
" 29,	0.43	0.30	0.25	0.33	0.34	0.38	0.44	0.36	0.43	0.36	0.32	0.35	0.33	0.30	0.31	0.43	0.35
" 31,	0.52	0.31	0.24	0.36	0.37	0.42	0.47	0.40	0.45	0.38	0.36	0.38	0.36	0.33	0.31	0.41	0.38
August 2, ...	0.57	0.34	0.26	0.39	0.40	0.45	0.51	0.42	0.49	0.40	0.40	0.41	0.40	0.36	0.36	0.45	0.40
" 4,	0.58	0.36	0.26	0.39	0.41	0.45	0.53	Damaged 0.44	0.51	0.41	0.42	0.42	0.42	0.37	0.35	0.45	0.40
" 6,	0.59	0.37	0.19	0.40	0.42	0.46	0.52	0.36	0.51	0.41	0.43	0.42	0.42	0.37	0.37	0.45	0.41
" 8,	0.55	0.37	Drying, damaged at base	0.40	0.42	0.48	0.50	0.37	0.51	0.41	0.44	Accident.	0.42	0.37	0.36	0.45	0.42
" 10,	0.58	0.39	..	0.40	0.35	0.51	0.51	0.39	0.52	0.43	0.40	..	0.43	0.40	0.36	0.47	0.44
" 12,	0.59	0.38	..	0.38	0.33	0.49	0.50	0.40	0.52	0.42	0.49	..	0.43	0.41	0.35	0.44	0.44
" 14,	0.63	0.40	..	0.39	0.37	0.53	0.53	0.40	0.54	0.44	0.54	..	0.47	0.43	0.35	0.47	0.49
" 16,	0.64	0.43	..	0.40	0.40	0.60	0.56	0.40	0.55	0.46	0.56	..	0.50	0.44	0.38	0.49	0.49
" 18,	0.69	0.46	..	0.41	0.45	0.65	0.58	0.44	0.60	0.50	0.60	..	0.53	0.49	0.41	0.53	0.53
" 20,	0.68	0.48	..	0.42	0.46	0.68	0.60	0.43	0.63.	0.50	0.61	..	0.52	0.49	0.41	0.54	0.52
Total gain in weight ...	0.81	0.24	-0.17	0.10	0.19	0.36	0.26	0.13	0.25	0.19	0.32	0.12	0.24	0.20	0.13	0.19	0.24
No. of leaves..	18	14	..	18	14	22	18	6	16	9	16	7	13	14	11	10	6
Length of roots	3½ in.	2½ in.	2½ in.	2½ in.	7½ in.	6 in.	8½ in.	6 in.	3¾ in.	3½ in.	10 in.	4 in.	7½ in.	3½ in.	8 in.	1½ in.	6½ in.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

On a Case of Work produced by the Electric Current. By R. COLLEY (*Phil. Mag.* [5], i, 469—477).—The total quantity of energy becoming free in a galvanic cell (a Daniell element, for instance), by the solution of a gram of zinc, is a constant quantity independent of the time taken in dissolving the zinc. A portion of this energy is manifested under the form of heat in the circuit; another may appear as mechanical work done by the current. A direct consequence of the principle of conservation of energy is that this second portion can only exist and increase at the expense of the first, their sum being constant. Relying on the laws of Faraday and Joule, it can be proved theoretically that any work produced by the current is accompanied by the appearance in the circuit of a new electromotive force opposed to that of the pile. This result has been confirmed in all cases hitherto studied: in electro-magnetic motors, induction-currents weaken the primary current: the separation of the elements of a chemical compound is always accompanied by the manifestation of the electromotive force called polarisation, &c. The author says, if, on the contrary, the experiment can be arranged in such a manner as to employ external work to reinforce the primary current, the new electromotive force will be of the same sign as that of the pile, as if, for example, by the exertion of our arms, we were to impress on the electro-magnetic motor a motion in the opposite direction to that taken by it under the influence of the current. The author's aim has been to apply these principles to a case not hitherto investigated, and to confirm by experiment the existence of this force which at present cannot be classified among known electromotive forces, but as he thinks must be regarded as a new one. To illustrate his view, the author imagines the following experiment: the current of a Daniell element passes up through a vertical tube filled with a solution of silver nitrate, entering and issuing from the liquid by electrodes of silver, and traversing a galvanometer. A quantity of silver, equivalent to the zinc in the pile, will dissolve at the lower and be deposited at the upper electrode; this transport of the metal upwards constituting the work done by the current. This work is, however, accompanied by work of opposite sign due to the opposite transport of the atoms previously combined with the silver; this being manifested by a diminution of concentration of the salt in the immediate vicinity of the negative, and of corresponding augmentation near the positive electrode. For most salts (including silver nitrate) this work is found to be less than the transport of the metal; there are, however, two iodides, zinc and cadmium, in which the opposite occurs. Having

seen that all work produced by the current or supplied by external forces serving to reinforce the current, is accompanied by the appearance of a new electromotive force, in the first case, the electromotive force, designated by the author e , will have the opposite sign, in the second case, the same sign as that of the pile E . Thus, in a column of silver nitrate, an ascending current will be feebler than a descending one, for in a circuit of equal resistance, there will be in the first case an electromotive force $E - e$, in the second, $E + e$; the inverse will take place with cadmium iodide. The following are given by the author as the final values of the electromotive force for a column of one meter :—

Silver nitrate	$e = 0.000005195$ Daniell
Cadmium iodide	$e = 0.000015670$ „

The apparatus employed consisted of a glass tube filled with the solution of the electrolyte, closed at one extremity, communicating at the other with an air-pump by means of an india-rubber tube which could be closed by a pinchcock, and having the electrodes sealed into two lateral tubes. The tube was suspended through its centre of gravity, so that either end might be turned upwards. Tube No. 1 had a length of 1.6 meter, and when filled with solution of silver nitrate, had a resistance of 774 Siemen's units; tube No. 2 had a length of 3.6 meters, and a resistance nearly double No. 1.

The author gives a series of tables of his results, having observed alternately the intensity of the proper current of the tube when ascending and descending through the liquids. The mean results are stated in the following tabular form :—

Silver Nitrate.

Table I.	Tube 1	Diff. D — A = 4.1
„ II.	„ 1	„ D — A = 4.5
„ III.	„ 2	„ D — A = 6.9

Cadmium Iodide.

Table IV.	Tube 2	Diff. A — D = 6.2
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A designates the ascending, D the descending current.

J. M. T.

Electro-chemical Deposition of Aluminium, Magnesium, Cadmium, Bismuth, Antimony, and Palladium. By A. R. M. BERTRAND (*Compt. rend.*, lxxxiii, 854—857).—*Aluminium* is deposited on a copper-plate in granules from aluminium-ammonium chloride. The deposit may be polished. Chlorine is evolved at the positive pole.

Magnesium.—An adherent homogeneous deposit of magnesium may be obtained by electrolysing magnesium-ammonium chloride with a very powerful current.

Cadmium.—A spongy deposit of cadmium is obtained from its chloride, to which a few drops of sulphuric acid have been added.

Cadmium-ammonium chloride gives a grey non-adherent deposit, chlorine being evolved; a similar deposit was obtained from cadmium-calcium chloride; cadmium bromide acidulated with weak sulphuric acid gives a coherent mass, susceptible of polish. If an iron wire be used as negative, and a copper wire as positive electrode, the cadmium is deposited in long brilliant needles. A good result is also obtained with acidified cadmium ammonium bromide. Cadmium-ammonium iodide yields a spongy mass. The sulphate gives a coherent deposit capable of receiving a fine polish; a non-coherent deposit was obtained from the double sulphate of cadmium and ammonium.

Bismuth.—Ammonium chloride is the best solution from which to obtain an adherent deposit. The solution should contain 25 to 30 grams per litre, and should be cold. With a single Daniell's cell, the deposit takes place slowly and to a small extent; with a Bunsen's element it is quickly formed and very adherent. When polished, it has a shade intermediate between those of antimony and oxidised silver. It is not altered in dry air.

Antimony separates well from its double chloride with ammonium at ordinary temperatures. The deposit is black, and may be advantageously used to replace platinum. When deposited from the chloride by a weak current on a fragment of antimony, the metallic layer has very curious explosive properties.

Palladium may be deposited from a perfectly neutral solution of palladium-ammonium chloride. W. R.

Ratio of the Two Specific Heats of a Gas. By C. SIMON (*Compt. rend.*, lxxxiii, 726—728).—The author states that, by assuming certain hypotheses as to the constitution of gases, he is able to deduce for the ratio of the two specific heats the exact value 7·5, or 1·40, the experimental numbers for simple gases being comprised between 1·39 and 1·42. The hypotheses in question are, that the molecules of a gas are identical among themselves; that each consists of four atoms (or smaller molecules) placed at the angles of a regular tetrahedron; that the atoms thus constituted rotate about their centres of gravity; and that their vibrations are insensible or non-existent. R. R.

Application of the Mechanical Theory of Heat to the Study of Volatile Liquids: Simple Relations between the Latent Heats, Atomic Weights, and Tensions of Vapours. By RAOUL PICTET (*Phil. Mag.* [5], i, 477—489).—In consequence of an abuse of formulae not translated into ordinary terms, expressing the relations connecting the various properties of volatile liquids, the author proposes in this paper to give some laws representing with sufficient exactness the notions at present held upon this subject. He commences by determining the principal factors for the problem. To put the problem in a comprehensible form, he supposes a reservoir which may be called A, containing any volatile liquid; a pump, B, draws off the vapour formed in A at a constant temperature t^0 and tension P, and forces it into another reservoir, C, at a temperature t' and pressure P', the liquid passing into the gaseous state in A with

the reverse in C. To complete the cycle, the liquid is to be brought back to its initial temperature, and a conduit-tube permits the liquid accumulated in C to return into the first reservoir, A. In the above operation, it must be supposed that $t' > t^{\circ}$ and consequently $P' > P$. For instance, taking one kilogram of ether at $t^{\circ} = 0^{\circ}$, its vapour is drawn off under tension P_0 , and forced into C at a temperature $t' = 20$ and under pressure P_{20} ; then one kilogram of ether is reduced from the temperature 20° to 0° in passing through the junction-tube D, the cycle being completed, since the ether has returned to 0° under the initial pressure P_0 . Thus, by means of Regnault's numbers and table, the two essential elements of the problem can be calculated—(1.) Heat absorbed in A by the return of the liquid from the temperature: t' to t° . (2.) The work expended by the pump B to obtain compression of the vapour from pressure P_0 to P_{20} , these two equations being entirely independent of each other, one of them giving heat-units, the other kilogram-meters. For the mathematical calculations, the author adopts the following symbols:— t° , temperature of refrigerant, A; t' , temperature of condenser, C; $\frac{1}{3} \frac{1}{4}$, co-efficient of dilatation of gases; P , maximum tension of the vapour at t' ; T , work done by the pump, B; c , specific heat of the liquid; d , density of the vapour at 0° referred to that of air; 1.293 kilogram-weight of a cubic meter of air; 10333 kilograms = atmospheric pressure on a square meter; λ , latent heat of the liquid at t° . The author proceeds to work out the mathematical reasoning by a series of five equations. He then gives a table showing the coincidence existing between the numbers calculated from their hypotheses and those furnished by experiment.

Liquid.	Boiling point.	λ Calculated.	λ Observed.	Derivative.
	°			
Water	100	533.9	536	0.0346
Alcohol	78.21	210	214.05	0.0325
Carbon sulphide	46	84	83.54	0.03189
Ethyl oxide	35	90.12	89.76	0.03563
Chloroform	60	60.73	61	0.03337
Benzene	80	92.9	92.26	0.03000
Ethyl chloride	10	92.8	92.1	0.03779
Oil of turpentine	155	65.6	68	0.0261
Mercury	350	71.6	77	0.02049
Sulphurous acid	-10	94.2	94.5	0.04374

The deviations are slight and may be explained by the anomalies of Mariotte's law and errors of experiment. From further mathematical reasoning, the author concludes that for two temperatures t and t' taken arbitrarily, the difference of the internal latent heats multiplied by the atomic weight is a constant number for all liquids, and then gives a table containing numerical verifications of his hypothesis. He finally draws the following conclusions:—

- (1.) Cohesion is a constant quantity for all liquids.

(2.) The derivate of the Napierian logarithm of the quotient of the tensions by the temperatures is constant for all liquids at the same pressure and temperature.

(3.) The latent heats of all liquids brought to one and the same pressure, multiplied by the atomic weight at the same temperature, gives a constant product.

(4.) For all liquids the difference of the internal latent heats at any two temperatures, multiplied by the atomic weight, is a constant number.

Also on comparing his investigations with Dulong and Petit's law on specific heats, one more relation can be established, viz. :—

(5.) The latent heats of all liquids are multiples of the specific heats.
J. M. T.

A pretended Relation between the Mechanical Equivalent of Heat and the Molecular Weights. By J. THOMSEN (*Deut. Chem. Ges. Ber.*, ix, 1355—1357).—This relation, which Klingel tried to prove (*Pogg. Ann.*, clviii, 160), is founded on the fact that the number 0.0699, which expresses the difference between the specific heats of air at constant pressure and at constant volume, is almost identical with that of the specific gravity of hydrogen. But this agreement is a mere accident, as will be easily seen. C. S.

Compressibility of Gases at Pressures less than one Atmosphere. By D. MENDELEJEFF and V. HEMILIAN (*Deut. Chem. Ges. Ber.*, ix, 1341—1345).—Hydrogen, air, carbon dioxide, and sulphur dioxide were examined at pressures varying from 650 to 20 mm., and it was found that when the pressure is diminished, $\frac{d(pv)}{dp} > 0$, instead of being = 0, or the compressibility is less than that required by Boyle's law. The value of $\frac{d(pv)}{dp}$ increases with a diminution of pressure, and is for hydrogen when p 400 mm. = 0.000002 and when p 120 mm. = 0.000010.

Carbon dioxide and sulphur dioxide show, at pressures not much below an atmosphere, negative deviations, but at lower pressures they become positive. Thus the following values were found for carbon dioxide :—

$p_0 = 635$ mm.	$p_1 = 200$ mm.	
$p_0 v_0 = 10000$ mm.	$p_1 v_1 = 10029$ mm.	
$p_0 = 190$ mm.	$p_1 = 64$ mm.	$p_2 = 22$ mm.
$p_0 v_0 = 10000$ mm.	$p_1 v_1 = 9996$ mm.	$p_2 v_2 = 9983$ mm.

To obtain concordant results it is absolutely necessary that the measurements of pressure, volume, and absolute temperature be correct within one ten-thousandth.

Air shows positive deviations below one atmosphere, they then become negative until 30 atmospheres, when, as Natterer has shown, they remain positive up to 100 atmospheres. Hydrogen always shows positive deviations at any pressure either high or low. C. S.

Determination of Vapour Densities. By J. W. BRÜHL (*Deut. Chem. Ges. Ber.*, ix, 1368—1376).—The use of steam in determining vapour-densities by Hofmann's method has the great advantage that there is no difficulty in obtaining a uniform temperature, because steam possesses a very great capacity for heat, and, moreover, no thermometer is required, the temperature of the steam being ascertained from the height of the barometer, and read off from Regnault's tables. By increasing Torricelli's vacuum and diminishing the weight of substance, the author has succeeded in determining the vapour-densities of bodies boiling at 250° by means of steam. The tube which he used had a length of 1.5 meter, an interior diameter of 18 mm., and was drawn out a little at the open end, in order to close it with the finger when filled with mercury. The vacuum thus obtained was 190 c.c. The tube was calculated as follows; about 820 mm. from the open end a mark was made with a file, and the tube filled up to it with mercury, which was weighed, and thus the capacity of the tube up to the mark found to be 185.513 c.c. The mercury was then put back and three times 15 c.c. of mercury were added and the increase in height every time determined, the mean being 57.467 mm., or 1 mm. = 0.261 c.c. The volume of vapour is therefore given by multiplying the distance of the mercury from the mark with 0.261, and adding 185.513.

After the tube is completely filled with mercury, it is inverted in the trough, which is kept completely filled in order to avoid differences of level, and then surrounded by an outer tube or jacket of about 30 mm. of diameter, and a length of 950 mm., through which steam is passed until the mercury remains constant; after measuring its height (*b*) the apparatus is allowed to cool a little, and then the substance is introduced and heated until the height (*b'*) is again constant. The pressure *B* is then found by the formula:—

$$B = \frac{b - b'}{1 + 0.000181 t}$$

The correctness of this equation is proved in the paper, to which is added a table containing the experimental numbers and the results, of which we abstract the following:—

	Dimethyl- aniline.	Camphor.	Parabromo- benzene.	Coumarin.
V. d. { Calculated	60.39	75.83	117.66	72.82
{ Found	61.04	76.65	117.66	70.96—71.85
B. p.	192°	205°	219°	291°
<i>b</i> - <i>b'</i>	21.2	18	95	18.4 20.2
Weight of substance	0.0214	0.0205	0.0181	0.017 0.0198

The density of the vapour of coumarin was determined in aniline-vapour.

C. S.

Chemical Affinity. By H. KOMMATH (*Deut. Chem. Ges. Ber.*, ix, 1392—1325).—The attraction of silver and chlorine is stronger

than that of sodium and chlorine. If the compounds thus formed are saturated, we must assume that chlorine has a different attractive force for each of the other 62 elements, and the number of chemical molecular forces would thus be $\frac{62 \times 63}{2} = 1953$. But if the affinity of

chlorine is always the same, sodium chloride is a non-saturated compound, and the same will be the case with most other compounds. This may be explained by the following hypothesis: different atoms possess different quantities of chemical affinity, but only potentially, i.e., the maximum is developed only under certain physical conditions, and when they are attracted by a force having the same intensity.

If an atom of sodium has the intensity na and chlorine cl , we have:—

$$cl > na,$$

and sodium chloride still possesses the free force $cl-na$, which, however, is too weak to attract another atom. In each chemical reaction potential energy is therefore converted into actual, and consequently if two compounds, AB and CD decompose each other:—



we have—

$$ab + cd > ac + bd.$$

This hypothesis explains the existence of compounds with water of crystallisation, so called molecular compounds, &c. C. S.

Capillary Affinity. By E. CHEVREUL (*Compt. rend.*, lxxxiii, 682).—The expression capillary affinity comprehends all the facts presented when a solid body unites with a gas, or a liquid, or with a solid dissolved in a liquid whilst the solid body maintains its original form; such an action is the removal of colouring matter from a solution by means of charcoal. The experiments to which this paper has reference concern the action of massicot on lime-water, strontia-water, and baryta-water. From the results it appears that if a precipitate, A, is very bulky in comparison with a body B, which would not be precipitated, if it were alone, by the body C which has precipitated A, the precipitate may carry down by capillary affinity more or less of the body B.

It is necessary, in studying actions of this kind, to take into consideration the causes which may act diversely in the cases where solid bodies are in contact with liquids. C. H. P.

The Limits between which Fire-damp can Explode; and some New Properties of Palladium. By J. J. COQUILLION (*Compt. rend.*, lxxxiii, 709).—Mixtures of marsh-gas and air in different proportions introduced into a eudiometer, and fired by the electric spark, gave the following results.

Marsh-gas 1, air 5. The spark is without effect.

Marsh-gas 1, air 6. Explosion occurs only in a succession of shocks. This is the first limit of possible explosion; the marsh-gas is in excess.

Marsh-gas 1, and 7, 8, or 9, of air give a sharp explosion. A lighted match will burn the gas, without producing any explosion.

With 12, 13, 14, 15 of air for 1 of marsh-gas, the explosion occurs, but grows gradually weaker.

With 16 of air the effect is reduced to a series of slight intermittent commotions. This is the second limit; the air is in excess.

Palladium heated to bright redness by the electric current, in a mixture of 2 vols. of oxygen and 1 of marsh-gas gives no explosion, though the bulk of the gases diminishes in the theoretical proportions. A flame causes a great explosion.

C. H. P.

Inorganic Chemistry.

Note on Ultramarine. By A. LEHMANN (*Deut. Chem. Ges. Ber.*, ix, 1376).—Philipp has stated that blue ultramarine is changed into green, on heating it with sodium sulphate and charcoal; this reaction was discovered by the author.

C. S.

Some Double-salts of Calcium Sulphate. By R. FASSBENDER (*Deut. Chem. Ges. Ber.*, ix, 1358—1363).— $\text{CaSO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$, is best obtained by dissolving so much of potassium sulphate in a saturated solution of calcium sulphate as would saturate the water of the latter in the cold. The salt separates in small silky needles.

$\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$ is prepared by dissolving 285 grams of ammonium sulphate in sufficient water to get 800 c.c. of solution, which is then saturated with calcium sulphate evaporated to 500—600 c.c., and filtered at 40—50°. It seems to form small rhombic prisms and to be isomorphous with the potassium compound.

$\text{CaSO}_4 + \text{K}_2\text{SO}_4 + 2\text{KCl}$ is formed by adding a small excess of potassium sulphate to a solution of calcium sulphate and potassium chloride, which has been saturated at 16°.

Calcium sulphate dissolves pretty freely in ammonium chloride and in potassium nitrate. 82 c.c. of a solution of the latter saturated at 15° dissolved at 15.5° 1 part, and 21° one part of gypsum dissolved in 69 parts.

In a saturated solution of magnesium sulphate, gypsum is absolutely insoluble.

C. S.

Reactions of Gallium. By LECOQ DE BOISBAUDRAN (*Compt. rend.*, lxxxiii, 824—825).—Gallium may be separated from aluminium by taking advantage of the greater solubility of gallium hydroxide in ammonia than aluminium hydroxide. When a mixture of gallium and aluminium chlorides is fractionated with sodium carbonate, although the first portions of the precipitate show the lines Ga α 417 and Ga β 403.1 with greatest intensity, yet the separation cannot be thus affected. Sodium carbonate does not precipitate indium till after gallium. If gallium were intermediate in qualities between indium

and aluminium, it should be precipitated after indium and before aluminium, or *vice versâ*. Slightly acid sulphate and chloride of gallium are not precipitated by an acid solution of ammonium acetate, but neutral salts of gallium become turbid. An excess of ammonium acetate renders the solution clear, and it does not again become turbid on boiling, at least if not diluted with a large quantity of water.

Gallium chloride is very soluble and deliquescent; its solution when concentrated is clear, but it turns turbid on dilution; the precipitate, which is doubtless an oxychloride, dissolves with difficulty in dilute hydrochloric acid. Hence, when it is desired to extract all the gallium from an insoluble substance, strong hydrochloric acid must be used as solvent.

If exactly enough hydrochloric acid be added to a solution of gallium to prevent its turning turbid when diluted, the solution grows turbid when heated, and becomes clear on cooling. The same is the case with gallium sulphate and its alums.

Crystals of gallium chloride have a powerful action on polarised light.

Gallium sulphate is not deliquescent. An alum was made by mixing ammonium and gallium sulphates. It crystallises when a particle of alum is placed in the solution. The existence of the alum is thus proved.

W. R.

Titanium Compounds. By C. FRIEDEL and J. GUÉRIN (*Ann. Chim. Phys.* [5], vii, 24—56).—This work was undertaken with the object of ascertaining the true position of titanium amongst the elements, the authors doubting the propriety of classifying titanium in the same group with silicon, as none of the crystal-forms in which titanic acid occurs resemble in any way that of crystallised silica; nor do the natural titanates resemble the silicates. This research is more particularly connected with the study of the chlorides, oxychloride, the lower oxides and the nitrides of titanium, and the results show that titanium and iron are closely related.

1. **TITANIUM CHLORIDES.**—*Dititanium hexchloride*, Ti_2Cl_6 , is best prepared by heating a mixture of metallic silver and titanium tetrachloride (in the proportion of one atom of the former to one molecule of the latter) in a sealed tube in a temperature of 180° to 200° . The mass partially dries up, and a garnet-red solid remains behind, which consists evidently of silver chloride and dititanium hexchloride, the following reaction having taken place: $2\text{TiCl}_4 + 2\text{Ag} = \text{Ti}_2\text{Cl}_6 + 2\text{AgCl}$. If the amount of silver taken exceeds the proportion given above, no dititanium hexchloride is obtained. This compound is insoluble in carbon disulphide, chloroform, benzene, carbon tetrachloride and titanium tetrachloride, but dissolves in water, forming a rose-coloured solution. On heating a mixture of silver chloride and dititanium hexchloride obtained by Ebelmen's method (*Ann. Chim. Phys.* [3], xx, 386) in a current of dry carbonic acid, tetrachloride of titanium distils over, and the silver chloride is reduced to metallic silver. On increasing the temperature, inverse reactions occur, the metallic silver reducing the tetrachloride, and the hexchloride thus formed reacting upon the silver chloride. The authors explain this remarkable reaction by

pointing to the fact of dititanium hexchloride being non-volatile, and consequently not distilling, at the same time decomposing into tetrachloride and dichloride (TiCl_2 , a compound which decomposes water at the ordinary temperature, and is a reducing agent of the greatest power), the latter reducing the silver chloride formed, and eventually causing complete conversion into tetrachloride. Zinc exerts a similar action upon titanium tetrachloride, only in a lesser degree than silver. The hexchloride absorbs oxygen when in contact with the air, being converted into titanous acid and tetrachloride; heated in a current of hydrogen at the temperature of boiling sulphur, tetrachloride distils over, and a black substance remains behind. Tetrachloride is not decomposed at the same temperature. Bromine acts upon the hexchloride more particularly when aided by a gentle heat. On distilling the resulting product, excess of bromine first passes over; then at 160° the greater part distils over, the distillate being a colourless liquid, which fumes in the air. An analysis of this liquid proved it to have a chemical composition corresponding with the formula, TiCl_2Br , and to be a titanium chlorobromide, as will be seen from the results obtained, viz. :—

Weight of liquid taken for analysis = 0.4168 gram.
 „ TiO₂ obtained = 0.1610 „
 = 20.97 per cent. of Ti. Theoretical amount = 21.14 per cent.

Weight of chloride and bromide of silver obtained = 1.2340 per cent.

1.2205 gram of this mixture reduced in a stream of hydrogen gave 0.857 gram of metallic silver; whence $\text{Cl} + \text{Br} = 78.52$ per cent. Theoretical amount = 78.86 per cent.

Titanium Dichloride.—After very numerous and mostly unsatisfactory experiments, the authors have devised the following process, which is divided into two parts, viz.: (1.) The preparation of hexachloride; (2.) The conversion of the hexachloride into dichloride; but in order to ensure success, there must be an entire absence of air and moisture during the conversion of the former into the latter. A tabulated retort of green glass is used and sealed to a green glass tube 40 to 50 centimeters in length, and of equal bore to the delivery-tube of the retort. At the end of the former tube is attached a tube bent downwards, passing into a receiver intended to retain the excess of titanium tetrachloride. The green glass tube is covered with platinum foil for a length of from 20 to 30 centimeters, and then placed in a gas combustion-furnace; the air which may be present is displaced by a current of perfectly dry and pure hydrogen passing through for several hours. When all the air is displaced, the tetrachloride of titanium is allowed to flow into the retorts from a funnel having the following construction. In a tubulure at the upper part a caoutchouc stopper is inserted, perforated with one hole, and passing through this hole is a glass rod which can be pushed down so as to close the stem of the funnel in order to stop the flow of liquid from the funnel, or on raising it to allow the liquid to flow out. On the side of the body of the funnel is fused another tubulure which serves for the replenishing of the funnel with tetrachloride; it is closed with a glass

stopper. Below the place where the glass rod closes the stem and at one side of it, there is a third tubulure which is connected with the hydrogen generating apparatus, or the carbonic acid apparatus, as the case may be. The green glass tube is heated to redness on the part which is covered with platinum foil, hydrogen passed through the apparatus, and the tetrachloride in the retort heated to boiling, when it is observed that fine hexagonal lamellæ of hexchloride are deposited on the cooler portion of the tube and even partially penetrate into the receiver. The process can be continued until a sufficient quantity of hexchloride has been obtained, care being taken that the tube is not completely stopped up with deposit by occasionally heating the spot. The apparatus is allowed to cool in a stream of hydrogen, and the latter is then replaced by dry carbonic acid gas. The green tube is separated by a file from the retort and its contents pushed into a matrass (previously filled with carbonic acid gas) by means of a thick platinum wire. The matrass has a lateral tube sealed to it for the exit of the gases, whilst the tubulure or mouth of the matrass is closed by a caoutchouc stopper through which a glass tube is inserted reaching to the bottom of the matrass, and serving for the delivery of the gases. A current of hydrogen is passed through the apparatus in order to displace the carbonic acid; it is then placed on a suitable sand-bath surrounded with tiles to prevent any cold draught, and heated to dull redness, when tetrachloride of titanium is evolved and carried along by the hydrogen. When this evolution ceases, the apparatus is allowed to cool in a stream of hydrogen, which is afterwards replaced by a stream of carbonic acid gas, and the contents of the apparatus are rapidly transferred to a tube filled with carbonic acid gas and sealed up. The titanium dichloride thus formed is a blackish powder, which is occasionally in the form of flakes, very unstable in air, and in the presence of moisture (with the latter it becomes lighter in colour). Thrown into water it hisses like red-hot iron and dissolves, a copious evolution of hydrogen being the result. On the addition of ammonia to this solution, a copious black precipitate is formed, hydrogen being evolved at the same time. The black precipitate gradually changes to blue, and eventually to white, and on throwing a few drops of water upon the dichloride (taking care not to moisten it completely), sufficient heat is generated to cause it to take fire in the air. On being heated in the air, the di-chloride burns like tinder, fumes of the tetrachloride being evolved, and titanous acid remaining behind. It is insoluble in ether, bisulphide of carbon and titanium tetrachloride, and on being heated gently with absolute alcohol hydrogen is evolved, and a yellowish liquid formed, which on the addition of ammonia furnishes a blue-black precipitate. Dry ammonia gas passed over the dichloride at a red-heat gives rise to the formation of a peculiar nitride, Ti_3N_4 , hydrogen being set free according to the following equation, $3TiCl_2 + 4NH_3 = Ti_3N_4 + 6HCl + 6H$. Bromine forms with the dichloride a fuming liquid, which boils at about 180° , and is probably $TiCl_2Br_2$. Some difficulty was experienced in obtaining the dichloride perfectly free from oxychloride of titanium ($Ti_2O_2Cl_2$), but the authors succeeded eventually in obtaining a pure product.

Oxychloride of Titanium, $Ti_2O_2Cl_2$, is met with generally in the preparation of titanium dichloride, especially when air and moisture have been present. The small reddish-brown lamellæ observed by Ebelmen (*Ann. Chim. Phys.* [3], xx, 391) occurring in the preparation of the hexachloride were supposed by him to be a protochloride of titanium, but were in reality oxychloride. The authors prefer to prepare it by passing a mixture of hydrogen gas and titanium tetrachloride over titanic acid heated to bright redness. A somewhat larger yield is the result of this process, and the oxychloride clothes the sides of the porcelain or glass combustion-tube with soft flocculent crystals which are rectangular plates, probably of the rhombic system. The oxychloride is not readily attacked by water, or by very dilute nitric acid in the cold; thus it can be separated from the dichloride by dissolving it in water and filtering, but at the same time it is always altered in appearance. The crystals of oxychloride allow a reddish-brown light to pass through them, and they are acted upon by ammonia, first becoming black and afterwards white, the crystalline form remaining intact. Hydrogen is given off when the crystals are acted upon by ammonia, and this fact proves that the oxychloride does not belong to the type of $TiCl_4$, but to that of the hexachloride, Ti_2Cl_6 . Titanium oxychloride is tolerably stable in air, but eventually becomes paler in colour and changes into titanic acid; heated in air it burns, forming titanic acid and fumes of tetrachloride. The analyses made were not as correct as might be desired, but the authors had very little substance at their disposal, and they are of opinion that a small quantity of titanic acid was mixed with the oxychloride. The formula $Ti_2O_2Cl_2$ corresponds with the following percentage composition:—

	Ti.	Cl.	O.
	49.26	34.97	15.76
Found ..	50.16	31.07	

Sesquioxide of Titanium.—It was observed that titanic acid which had been subjected to the action of a mixture of hydrogen and titanium dichloride (as in the preparation of the oxychloride), was changed into a copper-coloured substance with violet reflections, and exhibiting isolated crystals and groups of crystals. The porcelain combustion-tube is generally coated with this substance here and there with beautiful hexagonal plates of the same. This coating or deposit must not be confounded with another one of a deep brass-yellow, which occurs at the fore part of the tube, and which also exhibits red crystals, the latter being the nitride of titanium described further on. The hexagonal crystals are in reality sesquioxide of titanium formed from the reduction of titanic acid by hydrogen, and assisted in its crystallisation by titanium dichloride, which is also partially reduced by the action of the water formed in the above reactions. Thus the authors obtained pure titanium sesquioxide having a metallic lustre and a reddish-violet colour. The crystals were examined under the microscope and found to be isomorphous with the specular iron-ore from Elba, as the primary rhombohedron R , the scalenohedron $\frac{2}{3}R_3$ (?) modified by the basal terminal plane (a , of the authors) were

observed. The characteristic triangular striation was observed on the basal terminal plane caused by its oscillatory combination with an obtuser rhombohedron, and its lustre was not so brilliant as that of the two first-mentioned forms. Measurements of the crystals were made by means of a Wollaston's goniometer, although the crystals were only $\frac{1}{100}$ to $\frac{1}{1000}$ of a millimeter in size, and found to agree closely with those of specular-iron and ilmenite. Long ago G. Rose considered the sesquioxides of iron and titanium to be isomorphous, whilst Mosander supposed the combination TiFeO_3 to be isomorphous with Fe_2O_3 . The authors show by their investigations that ilmenite cannot be regarded as a simple mixture of the two isomorphous compounds Ti_2O_3 and Fe_2O_3 , as in that case the angle of FeTiO_3 would be the mean of the angles of Ti_2O_3 and Fe_2O_3 ; it therefore appears more reasonable to admit the existence of three isomorphous compounds, viz., Ti_2O_3 , FeTiO_3 , and Fe_2O_3 , which can intermix with each other. This isomorphism helps to explain the varying composition of titanic irons. It is evident from the above-mentioned isomorphism that a closer relation has been established between titanium and iron than was formerly supposed to exist. Titanic hexchloride and ferric hexchloride crystallise in the hexagonal system; a dichloride of titanium exists corresponding with ferrous chloride; Ti_2O_3 dissolves in sulphuric acid, furnishing a salt crystallising in hexagonal lamellæ and corresponding exactly with ferric sulphate; further, it will be seen that nitrides are formed of the two elements under the very same circumstances. There is also an analogy existing between the spectra of the two elements. Isomorphism also exists in a marked degree between the silicon and titanium compounds of oxygen and chlorine, as will be seen from the following table:—

		Corresponding iron compounds.
SiO_2	TiO_2	—
Si_2Cl_4	TiCl_4	—
—	Ti_2O_3	Fe_2O_3
Si_2Cl_6	Ti_2Cl_6	Fe_2Cl_6
—	—	FeO
—	TiCl_3	FeCl_2

Titanium sesquioxide is a copper-red powder, with violet reflections; it exhibits a play of colours corresponding with that observed on specular-iron, and is hard enough to scratch glass, but not quartz. Specific gravity = 4.601 at 100° . Boiling nitric acid does not act upon it, but boiling sulphuric acid does so, sulphurous acid and titanic acid being formed when the operation is carried out in the presence of air; if the air be excluded, a slight separation of free sulphur takes place owing to reduction. Hydrofluoric acid and nitro-hydrochloric acid dissolve titanium sesquioxide when assisted by a gentle heat; on heating it with caustic potash, hydrogen is evolved. If the sesquioxide be ignited strongly in the air it is converted into titanic acid, and this property was made use of in determining the composition of Ti_2O_3 . Weight of sesquioxide taken = 0.6640 gram. Weight of titanic acid obtained = 0.737 gram. Ti = 67.67 per cent. Theoretical amount for Ti_2O_3 = 67.56 per cent. If the sesquioxide contain an admixture

of nitride, the percentage of titanium is higher. On passing a stream of a mixture of dry hydrogen and chlorine gases over titanic acid heated to redness in a porcelain tube, sesquioxide is not obtained as might naturally be supposed, but a greyish-blue crystalline substance of homogeneous appearance, agreeing well with an intermediate oxide of titanium already obtained by Deville by a similar process, and to which he assigned the formula Ti_3O_5 .

Action of Titanium Dichloride, Chlorine and Hydrochloric Acid upon Titanic irons and on Mixtures of Titanic Acid and Oxide of Iron.—From the above statements, titanate of iron may be considered an intermediate compound between ferric oxide and sesquioxide of titanium, viz., Ti_2O_3 , $FeTiO_3$, Ti_2O_3 ; the authors therefore considered it highly probable that a chloride existed analogous to titanate of iron and intermediate between ferric hexchloride and titanic hexchloride, but they did not succeed in preparing it. When ferrous oxides are acted upon at a red-heat by titanium tetrachloride, ferrous chloride and titanic acid are formed. On passing chlorine over titanic iron heated to a dull redness, ferric chloride volatilises and crystallises in plates in the cool part of the tube, oxygen being evolved and titanic acid remaining behind. The authors propose to separate titanium from iron by this reaction, modifying it, however, by passing a mixture of chlorine and hydrochloric acid over the titanic iron, as it was found that a perfectly pure white titanic acid was thus obtained. The process is as follows:—The chlorine and hydrochloric acid generating apparatuses are connected by means of a T-piece, the free limb being attached to a hard glass combustion-tube drawn out at one end, and this extremity connected with an apparatus consisting of three bulbs partially filled with water. From the latter apparatus a long glass tube serves to conduct any escaping gas and for the condensation of traces of ferric chloride. The combustion-tube rests in a channel of platinum foil, and is also covered by platinum foil in such a manner that the covering foil can be lifted off from time to time in order to examine the porcelain boat containing the substance to be acted upon, and under the boat a little fine sand is placed to prevent it adhering to the soft glass. The combustion-tube is heated for about two hours (the first half hour at a red-heat), when the decomposition is generally completed, but it is not complete so long as the titanic acid in the boat has a yellow colour, and the heat must not be too great otherwise there will be a slight volatilisation of titanium. The ferric chloride formed is washed carefully out of the combustion-tube, bulbs and other tubes, and the iron estimated as ferric oxide; should the latter contain a trace of titanium, it is again treated in the manner described above and the residue of titanic acid weighed. As an example of the accuracy of this method the following analysis of titanic iron may be cited:—

Weight of substance taken....	0.4615 gram.	
Titanic acid obtained	0.2035 „	= 44.52 per cent.
Ferric oxide obtained	0.2750 „	= 59.58 „

44.52 per cent. of titanic acid combines with 39.08 per cent. of ferrous
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oxide (equal to 43.42 of ferric oxide), leaving a residue of 16.16 of ferric oxide; the result therefore is :

TiO_2 .	FeO .	Fe_2O_3 .
44.52	39.08	16.16 = 99.76.

Nitrides of Titanium.—Wöhler (*Ann. Chim. Phys.* [3], xxix, 175) stated that four nitrides of titanium existed, viz., Ti_3N_2 , TiN_2 , Ti_5N_6 , and Ti_3N_4 . The authors have re-studied these compounds and found that only three exist, viz., Ti_3N_2 , Ti_3N_4 , and Ti_2N_2 . The first nitride is found in the cupolas of blast-furnaces, occurring in cubical crystals; the second is obtained by heating ammoniacal dichloride of titanium in a current of ammoniacal gas; the third is obtained by the action of ammoniacal gas upon sesquioxide of titanium or titanous acid, and is analogous to the sesquioxide and to the hexachloride of titanium in composition.

Ti_2N_2 .—The authors prepared this compound in the following manner:—Perfectly dry ammoniacal gas is passed over one or two porcelain boats (containing fine powdery titanous acid and sesquioxide of titanium) placed in a combustion-tube, care being taken to prevent the admission of air by causing the gas to pass through a column of mercury one or two centimetres in length. The combustion-tube is heated for four or five hours in order to ensure the complete decomposition of the sesquioxide and titanous acid, as the process is slow and must be repeated several times before the nitride is obtained in sufficient purity.

By examination under the microscope small black specks are here and there discernible in the interior of the grains of the nitride. The specific gravity of Ti_2N_2 is 5.28 at 18°; it is an amorphous powder, or a deposit having a brass-yellow colour, and is easily decomposed into titanous acid on being ignited in the air at a high temperature. Ti_3N_2 can be obtained mixed with carbon on heating titanous acid at a red-heat in a current of cyanogen, but no compound resembling the product observed in blast-furnaces is thus obtained.

Ti_3N_4 is easily prepared by Deville and Wöhler's method (*Ann. Chim. Phys.* [3], lii, 97). The authors succeeded in obtaining it in reddish-violet crystalline crusts. Under the microscope the crystals appeared to be acute rhombohedrons. On being heated to redness in a current of hydrogen it decomposes easily into Ti_3N_2 , and it is found that this occurs with greater facility if dry ammoniacal gas is substituted for the hydrogen.

In conclusion the authors point out that the titanium compounds can be referred to three types of definite compounds corresponding with the chlorides TiCl_4 , Ti_2Cl_3 , TiCl_2 , and that a remarkable analogy exists between titanium compounds of the second type and ferric compounds.

C. A. B.

Evolution of Antimony from Stibnite by Nascent Hydrogen.
By W. M. SKEY (*Chem. News*, xxxiv, 147).—Antimony or arsenic sulphide placed in hydrochloric acid together with zinc evolves arseniuretted or antimoniuiretted as well as sulphuretted hydrogen.

W. R.

Silicotungstates of Cæsium and Rubidium. By R. GODEFFROY (*Deut. Chem. Ges. Ber.*, ix, 1363—1367).—*Cæsium silicotungstate*, $\text{SiW}_{12}\text{O}_{42}\text{Cs}_3$, is obtained as a white crystalline precipitate by adding cæsium chloride to an aqueous solution of silicotungstic acid. It dissolves at 26° in 20,000 parts and at 100° in 192—200 parts of water, and is insoluble in alcohol and water containing hydrochloric acid, but dissolves to some extent in ammonia.

Rubidium silicotungstate, $\text{SiW}_{12}\text{O}_{42}\text{Rb}_3$, is a very similar body but more soluble, 1 part dissolving at 20° in 145—150 parts and at 100° in 19—20 parts of water and very freely in ammonia; in alcohol and water containing hydrochloric acid it is insoluble.

In conclusion the author gives a table of the solubility of the salts of the alkali-metals, from which it appears that while the simple salts of rubidium and cæsium are more soluble than those of the other metals, the double-salts, as well as the silicotungstates, borofluorides, &c., are less soluble. C. S.

Action of Acids on Iron. By MM. TRÈVE and DURASSIER (*Compt. rend.*, lxxxiii, 744).—Bars of iron immersed in water acidulated with sulphuric acid, were found to have been attacked so as to present the fibres of the metal in relief; but when nitric acid was added to the liquid the surface of the metal became hollowed into grooves having no relation to the direction of the fibres, but following the course taken by the bubbles of gas which were liberated by the action of the acids. R. R.

Some Changes in the Physical Properties of Steel produced by Tempering. By A. S. KIMBALL (*Chem. News*, xxxiv, 81).—Experiments were made upon the behaviour of tempered bars under a transverse strain, when the following results were obtained:—

I. The modulus of elasticity decreases as the hardness of the steel increases; in other words, the harder the bar the greater the deflection produced by a given weight.

II. The increase of deflection in a given time is greater the harder the steel.

III. The immediate set increases with the hardness of the steel.

IV. A bar recovers from a temporary set with greater rapidity the harder it is. D. B.

Mineralogical Chemistry.

Some American Vanadium Minerals. By F. GENTH (*Chem. News*, xxxiv, 78—80).—1. *Roscoelite*.—Occurs in small seams 1-20th to 1-10th of an inch thick in a decomposed yellowish, brownish, or greenish rock. The seams are made up of small micaceous scales, a quarter of an inch long or smaller, and frequently arranged in stellate or fan-shaped groups. The specific gravity of the purest scales was found to be 2.938; lustre pearly; colour dark clove-brown to greenish-

brown. Before the blow-pipe it fuses to a black glass, colouring the flame slightly pink. With phosphorus salt it gives a skeleton of silicic acid, a dark yellow bead in the oxidizing flame, and an emerald-green bead in the reducing flame. It is only slightly acted upon by acids, but readily decomposes when heated in a sealed tube to 180° with dilute sulphuric acid, leaving the silicic acid in the form of white, pearly scales and yielding a deep bluish-green solution. With sodium carbonate it fuses to a white mass. The vanadium was determined in the mineral by titration with potassium permanganate. After the separation of the other elements the vanadic acid was reduced by hydrosulphuric acid to V_2O_4 , which, after expulsion of the excess of hydrosulphuric acid, was re-oxidized to V_2O_5 by the permanganate. No matter whether only a very minute quantity of sulphuric acid is present or a very large excess, it was found that the V_2O_4 is completely oxidized into V_2O_5 by this process. From the quantity of oxygen required for oxidation in both cases it was found that vanadium in the mineral is present as $V_6O_{11} = 2V_2O_3 \cdot V_2O_5$. The other elements were determined by the usual methods. The finely powdered mineral was dried over sulphuric acid for two days and the different samples gave the following results:—

(a.) *Purest Scales*.—One portion was dissolved in sulphuric acid and the quantity and state of oxidation of the vanadium determined, also the silicic acid and insoluble impurities; the latter were left behind on dissolving the silicic acid in sodium carbonate. A second portion was decomposed by sodium carbonate and nitrate, and a third, for the determination of the alkalis, by Smith's method.

(b.) Another sample, not so pure, was analysed by fusion.

(c.) Still more impure than (b), was analysed by dissolving in dilute sulphuric acid in a sealed tube, &c.; $\alpha\alpha$ is the result of this analysis, $\alpha\beta$, after deducting 11.45 per cent. of impurities. (d) was decomposed by dilute hydrofluoric acid; the material for analysis had not been dried over sulphuric acid. (e) was dried over H_2SO_4 for several weeks; a portion decomposed with sulphuric acid gave 5.37 per cent. insoluble silicates, 0.23 per cent. of gold, and 43.24 per cent. of silicic acid. The V_6O_{11} was determined by difference; a second portion was decomposed by fusion, giving the analysis in e.

Insoluble silicates, quartz, gold, &c.	a. [0.85]	b. —	c α . 11.45	c β . —	d. 8.91	e. [5.60]
SiO ₂	47.69	47.82	43.46	48.60	—	46.81
Al ₂ O ₃	14.10	12.60	10.52	11.76	—	15.78
FeO.....	1.67	3.30	2.03	2.27	—	1.58
MgO.....	2.00	2.43	1.74	1.95	—	2.31
CaO.....	trace	trace	0.20	0.23	—	trace
Na ₂ O (trace Li ₂ O).....	0.19	0.33	0.30	0.34	5.96	{ 0.60 8.89
K ₂ O.....	7.59	8.03	5.35	0.98		
V ₆ O ₁₁	22.02	21.36	20.50	22.92	—	20.16
Ignition.....	4.96	5.13	5.32	5.95	6.84	3.87
	100.22	101.00	100.87	100.00	—	100.00

A mineral very similar in composition, and perhaps a compact impure variety of roscoelite, is found associated with the scales.

2. *Psittacinite*.—This mineral, which was mistaken for a tellurate of lead and copper, proved on analysis to be a "hydrous" vanadate of lead and copper. It occurs in very thin cryptocrystalline coatings, sometimes showing a small mammillary or botryoidal structure, also pulverulent. Colour siskin-green ("psittacinus," siskin or rather parrot-green) to olive-green; fuses readily before the blowpipe to a black shining mass, and gives with fluxes the reactions of vanadium, lead, and copper. It is soluble in dilute nitric acid, the solution yielding on evaporation a deep red mass. It occurs sometimes associated with gold and small quantities of cerussite, chalcopyrite, and limonite, upon quartz, at several of the mines in Silver Star District, Montana, and its occurrence in these mines is looked upon as a favourable indication, for when it is met with, the vein becomes immediately or soon after rich in gold.

The following are the results of five analyses:—

	a.	b.	c.	d.	e.
PbO.....	41.36	50.17	42.89	27.12	42.38
CuO	14.34	16.66	14.72	9.75	15.03
V ₂ O ₅	14.64	19.05	15.87	9.96	15.77
H ₂ O.....	7.42	—	Not deter.	—	7.25
SiO ₂	15.13	7.60	10.10	4.84	15.57
Al ₂ O ₃	1.29		3.83		4.00
Fe ₂ O ₃	2.72		2.19		
MgO	Not		0.65		
CaO.....	deter.		0.15		

D. B.

The Tripolite of Barbadoes. By T. L. PHIPSON (*Chem. News*, xxxiv, 108).—A most remarkable deposit of tripolite exists in the above-mentioned island, where it is mixed with carbonate of lime. Under the microscope it is found to be exceedingly rich in remains of fossil infusoria, the forms of which are very well preserved. The silica is hydrated and soluble to a great extent in potash, and, like tripolite from other localities, it constitutes an excellent polishing material. On account of its value in this respect tripolite has many imitations in commerce, but it can be recognized at once by analysis and also by the microscope.

The following figures give analyses of a Barbadoes sample, a Swedish sample, and two kinds of imitation tripolite met with in London:—

	SiO ₂ .	Fe ₂ O ₃ and Al ₂ O ₃ .	CaCO ₃ .	P ₂ O ₅ .	Moisture.	X*.
Barbadoes	71.50	2.32	10.60	0.08	5.66	9.84 = 100
Dagesfors, Sweden	78.00	6.15			15.85	= 100

* Combined water and trace of organic matter.

Imitations—

	SiO ₂ .	CaOCO ₃ .	Fe ₂ O ₃ , &c.	H ₂ O.
(1.)	1.0	88.4	5.6	5.0 = 100.00
(2.)	84.7	6.1		4.4 = 100.00

A sample of genuine tripolite from the Puy de Dome gave—

SiO₂, 87.2; H₂O, 10.0; Al₂O₃, Fe₂O₃, &c., 2.8.

Another sample from Algiers gave—

SiO₂, 80.0; H₂O, 9.0; Al₂O₃, Fe₂O₃, CaO, &c., 10.0.

In all cases the silica is mostly soluble in strong boiling alkali.

Barbadoes tripolite having been found a bad conductor of heat, it has been used with advantage for covering boilers. Boettger mentions that it will displace the aniline colours from their solution in spirit, and fix them so that after awhile the solution filters colourless.

D. B.

The Crystalline Form of Melinophane. By E. BERTRAND (*Compt. rend.*, lxxxiii, 711).—The form is found to belong to the right prismatic system, the crystals observed were truncated pyramids. The angular measurements are given. There is some reason to believe that the planes of separation which are found in the crystals, and which are practically parallel to the optic axis, are not true cleavage planes.

C. H. P.

The Formation of Meteorites, and Volcanic Agency. By G. TSCHERMAK (*Phil. Mag.*, [5], i, 497—507).—It is perhaps by an examination of the external form and internal structure of meteorites, rather than by chemical analysis, that we shall obtain further information respecting the origin of these extraordinary bodies.

Meteorites reach the earth in the form of angular fragments, which exhibit sometimes sharp, sometimes rounded edges, but possess no concentric structure even in their interior.

The angular nature of their faces is unquestionably due to fracture, and the fragment itself to the disruption of large masses of substance; the rounded edges and their external crust are not original characteristics, but can be proved to have been developed by the rapid transit of the meteorite through the atmosphere. An inspection of this crust has shown that during the latter stages of flight, disruption of the meteorite itself sometimes takes place. Guided by this examination, and by peculiarity of shape, Maskelyne succeeded in reconstructing a meteorite from fragments which fell many miles apart.

While the crystalline structure of many meteorites indicates that during the formation of their substance, considerable intervals of time for tranquil crystallisation at an uniform temperature must have elapsed, other specimens seem, on the contrary, to be composed of masses of angular fragments, resembling rather terrestrial breccias, or volcanic tuffs. These characters, together with the peculiar "slide" of terrestrial rocks, which is often observable in the structure of

meteorites, presuppose that the material of which they consist has been furnished by one or more large masses, the formation of which must have occupied a long period of time, but unfortunately it does not in any way account for the process of disintegration and disruption of the generating mass.

Passing over the older theories, which attributed the meteorite to the disruption by impact of planetary masses, the author attempts to show that, taking into consideration their fragmentary character and small size, it is more probable that they resulted from a pulverisation brought about by a force acting from within outwards; in short, by an explosion. He points out that, as is well known, an examination of the surface of the moon shows that it has passed through a stage of volcanic activity much more intense than we have any experience of; that recent researches have shown that explosive phenomena and violent cyclonic movements are still noticeable in our cosmical system; and that therefore it is not unreasonable to suppose that other and smaller star-masses may in a similar manner continue to lose substance by constant projection of fragments into space, until at last they themselves are resolved into small portions, and traverse the universe in orbits of the most varied kind.

It has been already stated that although many meteorites appear to result from a gradual and tranquil crystallisation, the majority on the contrary are made up of minute flakes and splinters, and of rounded granules. These granules, which were termed by Rose "*chondra*," present the following features, which enable us to recognise their mode of formation.

1. They are imbedded in a matrix, consisting of fine or coarse splinter-like particles.
2. They are invariably larger than these particles.
3. They are always distinct individuals, never merging into each other or joined together.
4. They are quite spherular when composed of a tough mineral, in other cases merely rounded in form.
5. They consist sometimes of one mineral, sometimes of several minerals, but always of the same material as the matrix.
6. The structure of the interior of the spherule is in no way related to its external form.

Precisely similar *chondra* are met with in terrestrial volcanic tufts, and therefore we are justified in supposing that these meteoric *chondra* owe their origin to a similar cause. They would therefore be the result of volcanic trituration, and owe their form to a prolonged explosive activity in a volcanic "throat," where rock-masses have been broken up, and the tougher particles not pulverised but rounded by continued attrition.

A good deal more evidence of a similar character is advanced by the author in support of his views of formation; he alludes to the finding of hydrogen in meteoric iron as proof that permanent gases and perhaps vapours, which are the great agents in transmitting volcanic energy, have played some part in the formation of these bodies; and although it may ever be impossible to obtain direct evidence of the volcanic activity which is supposed to have hurled these mysterious

masses of stone and metal into space, yet such evidence as the violent gaseous upheavals on the solar surface; the more feeble action of our terrestrial volcanoes; and the stupendous eruptive phenomena of which the lunar craters tell the history, nevertheless lend powerful support to any theory which assumes that meteorites owe their formation to volcanic agency.

J. W.

The Pitted Surface of Meteorites. By N. STORY-MASKELYNE (*Phil. Mag.*, [5], ii, 126—131).—In the *Compt. rend.* for April, 1876, Daubrée offered an explanation of the hollows which characterise the crusted surface of meteorites. This explanation he partly draws from the very singular parallelism between this alveolar surface of meteorites and that presented by the fragments of unburnt gunpowder that fall at some distance from the muzzle of a large piece of ordnance. The author, considering that Daubrée's explanation is not the most satisfactory way of accounting for phenomena so similar, brings forward an opinion of his own.

The fragments of powder alluded to are generally about the size of a small nut, and often very irregular in form. They present this peculiarity, that the surface is usually covered with a sort of irregular reticulation, composed of hollows, which though sometimes isolated, and nearly hemispherical, more often become confluent while remaining comparatively shallow. This appearance is so strikingly similar to that presented by the black incrustated and indented surface of an ordinary meteorite, that it naturally leads one to suppose that the resemblance is not accidental, but that it is due to a similar cause; more especially as in each case we have an accompaniment of detonation with enormous velocity, and sudden difference of temperature and pressure.

There can be no doubt that the fragments of gunpowder are the cores of some of the cubes of powder which, owing to the sudden removal of the vast pressure within the gun, have not had time to be entirely consumed. Owing to want of perfect homogeneity in composition, the combustion proceeds at the surface of the fragments at different centres of ignition, while the depth to which it penetrates depends on the density of the powder and the pressure exerted on it by the surrounding gases.

To take the case of a meteorite. The heat produced by atmospheric resistance fuses the surface of the stone or iron; the fused and oxidised material is thrown off as rapidly as it is formed, and the heat quickly begins to penetrate towards the interior of the mass. It is then supposed that the want of homogeneity in the mass permits the heat to penetrate from the exterior more rapidly in some places than in others, so that the sudden expansion due to the almost instantaneous accession of enormous temperature on the surface of the stone tears out small pieces of it, flings them away from the swiftly moving mass, and thus produces the peculiar pit-like depressions, the formation of which is under discussion.

It is possible that the greater fusibility of some than of other of the ingredients of the meteorite, may in certain cases explain some of these indentations; and again the difference in combustibility of the various

constituents, suggests another, and at first sight not unlikely cause of the phenomenon. However, the author thinks that the latter suggestion is not probable, since the most readily oxidisable constituents of a meteorite remain invariably unoxidised, and he has further noticed that carbonaceous meteorites are not more pitted, or even so much so, as meteorites containing no carbon. The view held by Daubrée is that the hollows are produced on the surface of the meteorite, by a sort of boring action effected by the air compressed and fiercely agitated into gyratory motion by the rapidly moving stone. The author observes that if this explanation were correct, we should without doubt find traces of the rotatory action in a whorl-like distribution or marking of the crust; such markings, however, are absent, and the view is at best rather improbable. He considers that the explanation offered above, viz., that the pitting is due to difference in the mechanical facility with which the sudden heat penetrates the mass at different points on its surface, may be fairly considered as the most probable solution of the question at issue.

J. W.

Contribution to the History of the Old Sulphur Well, Harrogate. By T. E. THORPE (*Phil. Mag.* [5], ii, 50—58).—After a brief historical sketch of the earlier analyses which have been made of the Harrogate waters, the author proceeds to detail the results of his own work in connection with the same subject, which was executed in 1875.

The water when drawn from the well was clear and colourless; smelled strongly of hydrogen sulphide, and had a decided alkaline reaction. Having stood a few hours it became turbid from separation of sulphur, but after a while it again became clear, and acquired a faint yellow tinge.

The rate of flow of the spring was calculated at 30 gallons per hour. Its temperature at time of collection was 10° C., but this temperature varies at considerable intervals, having been recently as low as 8°.

Specific gravity at 16·8° = 1011·04.

Determination of total Sulphur.—A known quantity of the water was mixed with bromine immediately after being taken from the spring. After standing, the barium sulphate was filtered off and weighed.

Determination of Sulphur oxidisable by Iodine Solution.—These determinations were made at the well in the usual manner with standard iodine solution and starch. The results were identical with those obtained by the use of bromine as before mentioned, and showed that no thiosulphate was present.

Determination of the Sulphur as Hydrogen Sulphide, and as Alkaline Sulphide.—A current of hydrogen gas was passed through the water, and the hydrogen sulphide expelled; the escaping gas was conducted into an ammoniacal solution of silver nitrate, and the resulting silver sulphide collected, converted into chloride, and weighed. From the weight thus obtained, the amount of sulphur present as hydrogen sulphide was calculated. By deducting the free hydrogen sulphide from the total weight of sulphur calculated to represent hydrogen sulphide, the amount of combined sulphur was obtained. Carbon oxy-

sulphide, which is said to exist in certain Hungarian sulphur-waters, was searched for, but with a negative result.

The following table exhibits the results in grains per gallon, of the principal analyses which have been made of the water of the Old Sulphur Well. We are thus enabled to trace the nature of the changes which the spring has experienced from time to time.

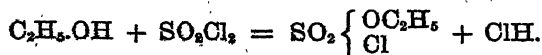
Analyst	West.	Hunter.	Hofmann.	Muspratt.	Davis.	Thorpe.
Date	1823.	1830.	1853.	1867.	1872.	1875.
Temp.	—	—	48° 2' F.	—	48° 9' F.	48° 2' F.
Sp. gr.	1013·24	—	1011·13	—	1011·16	1011·04
Lime	39·8	43·5	48·243	46·233	—	38·697
Magnesia	14·7	18·0	23·446	27·392	—	23·839
Baryta	—	—	—	3·68	—	4·833
Lithia	—	—	—	—	—	0·266
Potash	—	—	33·869	44·165	—	6·063
Ammonia	—	—	—	—	—	0·328
Soda	484·0	471·0	474·05	470·63	—	477·022
Chlorine	628·9	608·0	650·38	654·90	615·62	613·77
Bromine	—	—	trace	trace	—	1·985
Iodine	—	—	trace	trace	—	0·103
Sulphur	—	—	6·353	6·737	6·412	6·532
Carbon dioxide	—	—	—	—	—	35·404
Silica	—	—	0·241	—	—	0·703
Sulphuric acid	—	absent	0·101	absent	—	absent
Residue on evaporation...	1024·8	1016·0	1095·91	1108·78	1046·56	1047·013
Free H ₂ S	—	—	5·81	7·01	—	10·16
Free CO ₂	—	—	22·03	15·55	—	40·10
Total in cubic inches.....	36·4	34·0	36·09	—	—	—

The most striking alteration is shown in the quantity of potash, which is less than one-seventh of the amount observed in 1867. The proportion of bromine, however, has increased. The amount of barium salt in the water is large, and appears to be increasing: it is therefore desirable that it should be determined from time to time, since the presence of this element in large proportion must undoubtedly exercise considerable influence on the therapeutic action of the water.

J. W.

Organic Chemistry.

Action of Sulphuryl Chloride on Alcohols. By P. BEHREND (*Deut. Chem. Ges. Ber.*, ix, 1934—1938).—When one mol. of alcohol is added, drop by drop, to one mol. well-cooled sulphuryl chloride, a brisk reaction sets in, and the chloride of ethylsulphuric acid is formed.



It is a colourless oily liquid, possessing a very pungent smell. But if sulphuryl chloride be added to alcohol, ethyl sulphate is formed as well as its chloride and ethyl chloride.

By acting on the chloride of ethylsulphuric acid with methyl alcohol, the mixed ether, $\text{SO}_4 \left\{ \begin{array}{l} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{array} \right.$, is obtained as a yellowish neutral liquid, which water resolves into methyl alcohol and ethylsulphuric acid.

Sulphuryl chloride acts very violently on methyl alcohol; the chloride, $\text{SO}_2(\text{OCH}_3)\text{Cl}$, thus formed, resembles the corresponding, but is more easily decomposed by water. On acting upon it with methyl alcohol, a mixed sulphate is obtained, which is identical with that described above, yielding with water ethylsulphuric acid and methyl alcohol.

The chloride of butylsulphuric acid, when freshly prepared, is a colourless liquid, which soon turns brown and changes into a viscous liquid. The compound obtained by the action of sulphuryl chloride on benzyl alcohol is so unstable that it could not be obtained in a pure state. C. S.

Reciprocal Action of Oxalic Acid, and the Monatomic Alcohols. By A. CAHOUS and E. DEMARÇAY (*Compt. rend.*, lxxxiii, 688).—It appears from experiment that the reciprocal action of dry oxalic acid and the primary alcohols of the first series, gives rise to the formation of oxalic and formic ethers.

This occurs, also, with the primary alcohols of the second series, since allylic alcohol, by similar treatment, yields a mixture of oxalo- and formio-allylic ethers.

Benzyl alcohol was likewise completely etherified, the oxalate formed being solid and crystallisable. It boils at a very high temperature, and is changed by ammonia into oxamide, while benzyl alcohol is regenerated.

When oxalic acid acts upon a mixture of propylic and isopropylic alcohols, propylic oxalate is almost exclusively formed, and if this is saponified, a mixture of the alcohols rich in normal propylic alcohol is obtained, which, when again etherified by oxalic acid, furnishes nearly pure oxalate of propyl. This affords a method of separating the two alcohols. C. H. P.

Limited Oxidation of Essential Oils and Preliminary Report on the Ethers. By CH. T. KINGZETT (*Chem. News*, xxxiv, 127 and 135).—*A. Oxidation of Turpentine.*—It has already been mentioned that turpentine yields, when oxidised in a current of air in presence of water, peroxide of hydrogen, together with camphoric acid, acetic acid, camphor, and certain other less defined substances, the oil itself increasing in density and containing certain oxidised bodies, among which is a quantity of camphoric peroxide. The rate at which this oxidation takes place is very slow at first, and is indicated by the estimation, from hour to hour, of the peroxide of hydrogen which is formed; but when once the oxidation has fairly set in, it proceeds more rapidly, with increasing production of peroxide of

hydrogen and the other products, the amounts of which are simply limited by that of the turpentine itself. If no fresh turpentine be added to that already in operation, there will come a time when the percentage of hydrogen peroxide is at a maximum, and then, if the blowing be continued after that time, it slowly diminishes, in fact, at about the same rate that it forms. If, on the other hand, fresh turpentine be added, the oxidation proceeds as rapidly as ever, while there is no limit to the quantity of peroxide formed. The slow rate at which the oxidation of fresh turpentine proceeds, the greater rate it attains after the turpentine has been changed, and the increase in density of the turpentine is exemplified by the following figures:—

		Grams of H_2O_2 in 100 c.c. solution.	
A.	After 37 hours	0.0651	gram H_2O_2 .
	" 58 "	0.4500	"
			0.864 originally.
B.	" 24 "	the spec. grav. of the oil = 0.880	
	" 44 "	" " = 0.949	

By the following determination, the increase in the boiling point of the oil as the oxidation proceeds is illustrated:—

Original oil.	Oil after 24 hours' oxidation.	After 27 hours' oxidation.
10 p. c. at 157° C.	at 162° C.	at 165° C.
20 " " 159 "	" 165.5 "	" 166 "
30 " " 160 "	" 168 "	" 170 "
40 " " 160 "	" 171 "	" 171 "
50 " " 160.5 "	" 174 "	" 174 "
60 " " 161 "	" 181 "	" 185 "
70 " " 162 "	" 193 "	" 206 "
80 " " 164 "	" 210 "	—
90 " " 166 "		

B. Antiseptic and Disinfecting Powers of the Solution.—The above-described solution possesses great power as an antiseptic and disinfectant; this property is not, however, entirely dependent upon the peroxide of hydrogen contained, but relates also to the camphoric acid and other constituents. White of egg, milk, and beer are kept fresh for some considerable time. For 35 c.c. of substance from 1.75 to 4 c.c. of antiseptic were used. From a series of experiments undertaken with the view of ascertaining to which constituents of the solution the antiseptic and disinfecting character is to be ascribed, it was found that its power is distributed between the peroxide of hydrogen and camphoric acid, but the former of these is able to evolve large quantities of oxygen, which, in this state, is nascent, and of a powerful oxidising character.

C. Oxidation of the Ethers.—Former researches by the author seemed to show that all the members of the terpene family of the formula $\text{C}_{10}\text{H}_{16}$ give peroxide of hydrogen by atmospheric oxidation, and that this property is, no doubt, related to cymene, $\text{C}_{10}\text{H}_{14}$, which, as obtained

from various sources, also yields peroxide of hydrogen, so that any hydrocarbon containing cymene [paramethyl-propyl-benzene, $C_6H_4(CH_3)(C_3H_7)$], as a proximate nucleus would presumably give peroxide of hydrogen under suitable treatment. Thus, it was possible to produce a large quantity of peroxide of hydrogen by oxidation in a current of air at 60° in presence of water from menthene, $C_{10}H_{18}$, a small quantity of which the author obtained from Dr. Wright. For Wright has, by the action of bromine on methenes, succeeded in obtaining a terpene, from which, on further bromination, cymene was produced. It was further demonstrated that clove terpene, $C_{15}H_{24}$, by the fact of its failing to give peroxide of hydrogen in oxidation, does not contain cymene as a proximate nucleus, which fact Wright has supported by showing that clove terpene gives no cymene by the action of bromine. Regarding cymene as a hydrocarbon constituted of proximate nuclei, the author was led to consider the possibility of obtaining peroxide of hydrogen by the atmospheric oxidation of suitable compounds containing methyl, propyl, &c. And for the obvious reason that the ethers may, in a certain sense, be considered as oxides of the hydrocarbon radicles of the marsh-gas series, the author fixed upon them for his first experiments.

Ordinary ethylic ether has long been credited with the power of producing ozone, but beyond this, at the time the author commenced his investigations, the subject was in a state of mystery similar to that which surrounded the so-called formation of ozone by the oxidation of essential oils. That is to say, nothing was known about it, beyond that there had been recognised under these conditions a principle which was mistaken for ozone, and of whose production there was no reasonable theory.

Ethylic ether gives, apparently, by atmospheric oxidation, acetic ether and certainly peroxide of hydrogen, the latter having been obtained in estimable amount. The reaction which takes place may be explained as follows:—

- (1.) The oxidation of ether into acetic ether and water.
- (2.) The oxidation of acetic ether into the anhydride and that into the peroxide.
- (3.) The decomposition of the latter with water, simultaneously with its formation.

The formation of acetic peroxide in the above case is similar to that which takes place in Brodie's method of preparing that body by acting on acetic anhydride with barium peroxide. It appears that ordinary atmospheric oxygen plays the same part in these experiments as the oxygen of the barium peroxide in Brodie's method. This fact would give strength to the author's theory regarding the formation of peroxide of hydrogen from turpentine, which may be represented as its oxidation into camphor (corresponding to ether), then the oxidation of this body into camphoric anhydride, and of the anhydride finally into the peroxide, which is slowly decomposed by water.

In conclusion, it is stated that the above method of experiment will be applied to all the ethers available. Meanwhile, the preliminary results in this new direction already foreshadow a system of classification of the terpene derivatives. The production of peroxide of

hydrogen from camphoric peroxide and acetic peroxide amounts to a demonstration of the existence of the radicle hydroxyl in these compounds, and in a certain sense may be considered as the isolation of hydroxyl itself. D. B.

Isomeric Sulphine-compounds. By F. KRÜGER (*Journ. pr. Chem.* [2], xiv., 193—213).—I. *Compounds of Diethylmethylsulphine.* The ethyl sulphide used for this investigation was obtained by treating alcoholic potassium sulphide with ethyl chloride, which was prepared by Groves' method. If to one part of zinc chloride only one and a half of alcohol be taken, and the mixture heated from the beginning, a large quantity of ether is always formed, which is avoided by using at least two parts of alcohol and heating the solution after it has been saturated with hydrochloric acid in the cold.*

When equal numbers of molecules of ethyl sulphide and methyl iodide are heated with a little water on a water-bath, diethylmethylsulphine iodide is obtained as a reddish-brown syrupy liquid, which does not crystallise, and when heated gives off the smell of ethylsulphide. On shaking it with moist silver chloride, the corresponding chloride is formed, which dries up in a vacuum to a pale syrup. The hydroxide, which was obtained by decomposing the iodide with moist silver oxide, refuses also to crystallise, and is a powerful base; the nitrate and sulphate crystallise in a vacuum in long, deliquescent needles; the oxalate and picrate could not be obtained in crystals.

On adding platinic chloride to a solution of the chloride, the compound $(S(C_2H_5)_2CH_3Cl)_2PtCl_4$ is obtained as a pale red crystalline powder, which is sparingly soluble in cold water, and insoluble in alcohol and ether. From hot water it crystallises in cubes, octohedrons or tetrahedrons, which on drying crumble to a powder. The salt melts at 214° with decomposition.

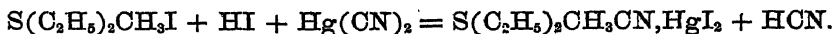
$S(C_2H_5)_2CH_3Cl \cdot AuCl_3$ is readily soluble in alcohol, ether, and hot water, and crystallises in long pale yellow needles, melting with decomposition at 192° .

$S(C_2H_5)_2CH_3Cl \cdot 6HgCl_2$ is a thick, white crystalline precipitate, which is sparingly soluble in cold water, alcohol, and ether. It crystallises from hot water in prisms resembling rock-crystal and melting at 198° without decomposition, which takes place only at a higher temperature.

When a solution of the crude iodide containing hydriodic acid is mixed with a hot solution of mercuric cyanide, the smell of carbamines and hydrocyanic acid is given off, and a yellow oil is precipitated, which solidifies on cooling, and is insoluble in all solvents. But when cold solutions are mixed, only hydrocyanic acid is evolved, and yellow, quadratic crystals separate out, which are insoluble in alcohol, ether

* *Abstracter's note.*—Krüger says that this observation agrees with mine, inasmuch as on preparing amyl chloride I obtained only a small yield, but much amyl ether, and therefore I considered Groves' method not to be fit for obtaining the homologues of ethyl chloride. This is however a mistake; I obtained only a little ether and a good yield of chloride, which was a mixture of the primary and secondary; and for this reason Groves' method is not adapted for the preparation of the homologues.

and carbon sulphide, and very slightly soluble in water; on evaporating this solution, the compound remains as an amorphous mass. Its formula is $S(C_2H_5)_2CH_3CN, HgI_2$, and it is formed according to the equation:—



It melts at 115° , and a few degrees above it decomposes into mercuric iodide, a carbamine, and a liquid smelling like ethyl sulphide.

When it is treated with hydrogen sulphide in presence of water, mercuric sulphide is formed, which undergoes the known changes of colour, and on continuing the action of the gas, becomes at last red, being converted into cinnabar, which on heating sublimes as a black mass, yielding again a red powder. Analogous compounds of sulphine-cyanides and mercuric iodide give the same reaction, while the double mercuric sulphine chlorides give black mercuric sulphide.

In order to obtain pure diethylmethylsulphine iodide, a mixture of ethyl sulphide and methyl iodide was heated for some days to 120° , but the reaction proceeded according to the equation:



When trimethylsulphine iodide is heated with an excess of ethyl iodide to 150° , it is hardly changed, while on heating triethylsulphine iodide with methyl iodide, it is converted into trimethylsulphine iodide.

II. *Compounds of Ethylmethylsulphine*.—Ethylmethyl sulphide was obtained by acting with methyl iodide on sodium mercaptide; it boils at 65 – 66° , and not at 58.8 – 59.5° , as Carius has stated. On heating it with ethyl iodide and a little water, the compound $SC_2H_5.CH_3.C_2H_5.I$ is formed, which crystallises in a vacuum in long, very deliquescent needles.

The corresponding chloride does not crystallise, and the nitrate and sulphate are as deliquescent as the analogous salts of diethylmethylsulphine.

$(SC_2H_5.CH_3.C_2H_5.Cl)_2PtCl_4$ is a dark red crystalline precipitate which is insoluble in ether and alcohol, and crystallises from water in apparently monoclinic prisms, which on drying crumble down to a rose-coloured powder, and melt at 186° under decomposition. When it is repeatedly recrystallised or heated for some time with water, it is changed into the isomeric diethylmethylsulphine-compound.

$SC_2H_5.CH_3.C_2H_5.Cl.AuCl_3$ is a pale yellow crystalline powder, which is readily soluble in hot water, alcohol, and ether, and melts with decomposition at 178° .

$SC_2H_5.CH_3.C_2H_5.Cl.2HgCl_2$ is a white crystalline precipitate crystallising from hot water in rhombic plates, melting at 112° ; under water it melts below 100° , and does not then crystallise any more.

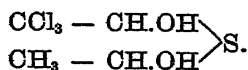
$SC_2H_5.CH_3.C_2H_5.ON.HgI_2$ is an amber-yellow precipitate consisting of apparently monoclinic prisms; it is insoluble in water, alcohol, and ether, and melts at 98° . When more strongly heated it yields mercuric iodide, a carbamine and a sulphide.

The results of this investigation prove that the sulphine-compounds

obtained by the combination of methyl iodide with ethyl sulphide are isomeric with those formed by combining ethyl iodide with methyl-ethyl sulphide. As these bodies are so very stable, and when heated are not simply resolved into their components, the author does not regard them as so-called molecular compounds, and comes therefore to the conclusion that their isomerism is caused by a difference between the four combining units of sulphur. C. S.

Combination of Chloral and Acetyl Chloride. By J. CURIE and A. MILLET (*Compt. rend.*, lxxxiii, 745—746).—Chloral and acetyl chloride combine when they are heated together for some time at 100°. The product is a liquid heavier than water, and insoluble in it, and boiling without decomposition at 186°. From this body nascent hydrogen removes two atoms of chlorine, and a new substance is obtained, insoluble in water, and boiling at 146° without decomposition. This substance is isomeric with acetate of dichlorinated ethyl, which boils at 125°, and also with dichloracetate of ethyl, which boils with decomposition at 156°. When it is warmed with zinc and acetic acid, aldehyde is formed. R. R.

Action of Potassium Sulphydrate on Chloral Hydrate. By A. MICHAEL (*Deut. Chem. Ges. Ber.*, ix, 1267).—When potassium sulphydrate is added in small quantity to an aqueous solution of chloral hydrate, the liquid becomes turbid from separation of sulphur, and after filtration deposits crystals of a compound agreeing in composition with the formula, $C_2H_5Cl_2SO_2$. This substance forms fine transparent colourless rhombohedrons, melting with decomposition at 96—97°. It possesses a peculiar mercaptan-like odour, and dissolves easily in water. It is decomposed by solution in water and by ammonia, and apparently also by the further action of potassium sulphydrate. The reactions of the body are consistent with the following constitutional formula:—



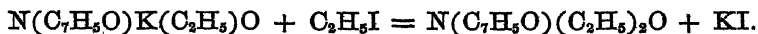
J. R.

Note on Reboul's Normal Pyrotartaric Acid. By W. DITTMAR (*Deut. Chem. Ges. Ber.*, ix, 1339).—The author some years ago obtained deoxyglutanic acid, which like its isomeride pyrotartaric acid, is not resolved by heat into carbon dioxide and butyric acid, and he then pointed out that one of these must be the normal compound. C. S.

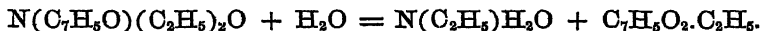
Ethers of Hydroxamic Acids, Ethylhydroxylamine, and Methylhydroxylamine. By W. LOSSEN and J. ZANNI (*Liebig's Annalen*, clxxxii, 220—230).—Ethylbenzhydroxamic acid was obtained by Eiseler as an oily body only. When prepared from pure materials, however, it crystallises in brilliant tables or prisms, which melt at 53·5—54·5°.

Ethyl-ether of Ethylbenzhydroxamic Acid.—This body is readily

formed by the action of ethyl iodide on ethylbenzhydroxamic acid is dissolved in alcoholic potash :



It is a yellowish, highly refractive liquid, of agreeable aromatic odour, insoluble in water, but easily soluble in alcohol and ether. When dissolved in weak spirit and heated with a little hydrochloric acid, it is resolved into ethylhydroxylamine and ethyl benzoate, thus :



The former product combines with the hydrochloric present to form

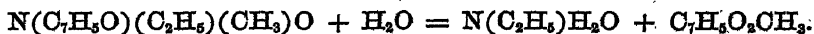
Ethylhydroxylamine hydrochloride, $\text{N}(\text{C}_2\text{H}_5)_2\text{H}_2\text{O}.\text{HCl}$, a crystalline substance which deliquesces in the air and dissolves easily in absolute alcohol. It is precipitated from its alcoholic solution in large pearly laminæ on addition of ether. When heated it melts and decomposes, evolving gas. Its solutions exhibit many of the reactions of hydroxylamine, reducing silver, mercury, and copper salts, and also chromic acid in alkaline solution. The *chloroplatinate*, $2[\text{N}(\text{C}_2\text{H}_5)_2\text{H}_2\text{O}.\text{HCl}] + \text{PtCl}_4$, formed by mixing alcoholic solutions of the hydrochloride and platinum tetrachloride, is deposited as a yellow crystalline powder on adding ether to the solution. It dissolves easily in water and absolute alcohol, and crystallises therefrom in prisms on evaporation.

Methyl-ether of Ethylbenzhydroxamic acid (*benzoxylmethylethylhydroxylamine*), $\text{N}(\text{C}_7\text{H}_5\text{O})(\text{CH}_3)(\text{C}_2\text{H}_5)\text{O}$, is obtained by the action of methyl iodide on ethylbenzhydroxamic acid in alkaline solution, in the same manner as the ethyl-ether, which it resembles in external characters. When treated with dilute hydrochloric acid it yields methylhydroxylamine and ethyl benzoate :



Methylhydroxylamine hydrochloride, $\text{N}(\text{CH}_3)_2\text{H}_2\text{O}.\text{HCl}$, formed in the reaction just mentioned, closely resembles the ethyl-compound. It crystallises from a hot saturated solution in alcohol in flat prisms. The *chloroplatinate*, $2\text{N}(\text{CH}_3)_2\text{H}_2\text{O}.\text{HCl} + \text{PtCl}_4$, dissolves very easily in water and alcohol. It is precipitated from its alcoholic solution by ether as a crystalline powder, and is deposited from its solutions on evaporation in large flat orange-red prisms or tables.

Ethyl-ether of Methylbenzhydroxamic acid (*benzoxylethylmethylhydroxylamine*), $\text{N}(\text{C}_7\text{H}_5\text{O})(\text{C}_2\text{H}_5)(\text{CH}_3)\text{O}$, formed by the action of ethyl iodide on methylbenzhydroxamic acid dissolved in potash, is metameric, not identical, with the methyl-ether of ethylbenzhydroxamic acid described above. It is a mobile liquid, of agreeable aromatic odour. By decomposition with hydrochloric acid it yields ethylhydroxylamine and methyl benzoate :



J. B.

Researches on the Ferrocyanides. By M. WYROUBOFF (*Ann. Chim. Phys.* [5], viii, 444—486).—This memoir relates to the insoluble ferrocyanides. They are described in alphabetical order, because the variations in the composition of the salts of metals of the same group are so great as to defeat any attempt at classification. In the formulæ throughout, the radicle FeCy_6 is represented by Cfy .

Aluminium ferrocyanide, $\text{Al}_4\text{Cfy}_3 \cdot 17\text{H}_2\text{O}$, is deposited after some time from hot concentrated solutions of yellow prussiate and an aluminium salt, when they are mixed, as a gelatinous, bluish-white precipitate. It is slightly soluble in pure water; on drying, it becomes horny, and resembles fused silver chloride.

Antimony ferrocyanide, $\text{Cfy}_3\text{Sb}_4 \cdot 25\text{H}_2\text{O}$, was not prepared by the author, who simply quotes Atterberg's results.

Bismuth ferrocyanide. (A), $\text{KBiCfy} \cdot 4\text{H}_2\text{O}$; (B), $\text{Bi}_2\text{Cfy} \cdot 5\text{H}_2\text{O}$. (A) was obtained by precipitating yellow prussiate with a moderately acid solution of bismuth nitrate. It occurs as a bulky, bright yellow precipitate, having a greenish tinge, and is slightly soluble in pure water. (B) is obtained by precipitating with hydroferrocyanic acid, instead of the yellow prussiate. It exactly resembles (A). In (A) the bismuth is triatomic; in (B) it is only diatomic.

Cadmium ferrocyanide, $\text{K}_5\text{Cd}_2\text{Cfy}_4 \cdot \text{H}_2\text{O} = 2\text{Cd}_2\text{Cfy} \cdot \text{KCdCfy} \cdot \text{K}_4\text{Cfy} \cdot \text{H}_2\text{O}$.—Whatever may be the proportions of the cadmium salt relative to the yellow prussiate employed, the composition of the ferrocyanide shown by the above formula remains unaltered.

When cadmium ferricyanide is dissolved in concentrated ammonia, fine red crystals are deposited after some days. They are absolutely insoluble in water, but dissolve in ammonia. Their composition is $(\text{FeCy}_6)_3\text{Cd}_3 \cdot 2(\text{NH}_4)_3\text{O}$. It is probable that the ammonia replaces water, as in the silver ferrocyanide.

Cerium ferrocyanides. (A), $\text{KCeCfy} \cdot 4\text{H}_2\text{O}$; (B), $\text{Ce}_2\text{Cfy}_3 \cdot 3\text{OH}_2\text{O}$. These formulæ are written upon the hypothesis of the triatomicity of the metal; if the metal be considered as diatomic, the formulæ would be $\text{Ce}_3\text{K}_2\text{Cfy}_3$, and Ce_3Cfy respectively. The same may be said of the metals lanthanum, didymium, erbium, and yttrium, whose ferrocyanides offer a great analogy to those of cerium.

Ferrocyanides of Cobalt.—(A.) $\text{Co}_2\text{Cfy} \cdot \text{K}_4\text{Cfy}$; deep violet. (B.) $2\text{Co}_2\text{Cfy} \cdot \text{CoKCfy} \cdot \text{K}_4\text{Cfy} \cdot 14\text{H}_2\text{O} = \text{K}_5\text{Co}_3\text{Cfy}_4$; pinkish-grey. (C.) $\text{Co}_2\text{Cfy} \cdot 7\text{H}_2\text{O}$; emerald-green. (D.) $\text{Co}_7\text{Cfy}_4 \cdot 22\text{H}_2\text{O} = 2\text{Co}_2\text{Cfy} \cdot \text{Co}_3\text{Cfy}_2$; greenish-grey.

These salts, with the exception of (B), resemble in properties and composition the corresponding salts of nickel. (A) and (B) are obtained by the yellow prussiate; (C) and (D) by hydroferrocyanic acid; (B) and (D) with an excess of the cobalt salt. (B) is insoluble only in presence of an excess of the yellow prussiate. The others are completely insoluble in water. They are readily decomposed by alkalis. (C) and (D) are readily transformed into (A) when heated with a solution of yellow prussiate.

Copper ferrocyanides.—(A), $\text{Cu}_2\text{Cfy} \cdot 10\text{H}_2\text{O}$, Hatchett's brown. (B), $\text{K}_2\text{Cu}_2\text{Cfy} \cdot \text{K}_4\text{Cfy} \cdot 12\text{H}_2\text{O}$, deep brown; crystallised. (C), $\text{KCuCfy} \cdot \text{H}_2\text{O}$, red-brown.

Hatchett's brown is soluble in yellow prussiate; the solution on eva-

poration deposits crystals, which have the composition, $K_3Cu_2Cfy. 6H_2O$.

Didymium ferrocyanide, $DKCfy. 2H_2O$.

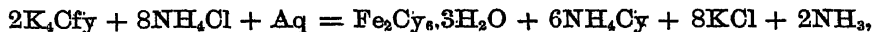
Erbium ferrocyanide, $ErKCfy. 4H_2O$.—This salt has been described by Clève and Hoeglund, but was not prepared by the author.

Iron Ferrocyanides.—The cyanides of iron, generally regarded as simple, when acted upon by alkalis, eliminate iron; and form ferro- or ferricyanides, for which reason the author regards them as double cyanides, containing the radicle, $Cfy (FeCy_6)$. The formula for iron percyanide would thus be $FeCfy$, and for the protocyanide, if it exists, Fe_2Cfy . The equation



illustrates the action of potash on the percyanide; and, in fact, the ferricyanide produced may always be found, although it rapidly changes to ferrocyanide in contact with the alkali.

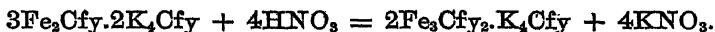
In the reaction given to explain the formation of iron percyanide—



2 molecules of ammonia are evolved, but under certain conditions they attach themselves to the percyanide, giving $(NH_4)_2FeCfy$, a body which is so stable that it can be decomposed only by fusion into potash. This formula is parallel with that of Williamson's ferrocyanide of potassium and iron, obtained by the action of weak sulphuric acid on potassium ferrocyanide; or, as is here shown, by precipitating potassium ferrocyanide with a ferrous salt; but Williamson's formula is regarded by the author as inexact, the correct formula being $3Fe_2Cfy. 2K_4Cfy$.

This body is very unstable, and is soluble in water, but not so in water containing ammonium chloride. When thoroughly shaken with ammonia, though not decomposed, it becomes violet, and on standing for some time returns to white. This experiment may be repeated several times.

By treating the white salt with nitric acid, Williamson obtained a violet-blue salt, which he described as ferricyanide of iron and potassium, but the analyses here given lead to the formula, $K_4Fe_3Cfy_2 = 2Fe_3Cfy_2.K_4Cfy$; the reaction is shown by the equation—



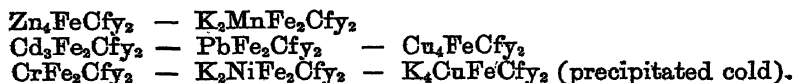
The inverse reaction is easily effected, for by heating the violet salt with excess of yellow prussiate, the white salt is formed, and potassium ferricyanide set free.

Ferric salts yield with potassium ferrocyanide two different compounds, according to the proportions employed, namely, soluble blue, $K_3Fe_3Cfy_6$, and Prussian blue, Fe_3Cfy_6 . The former has been generally viewed as a double ferrocyanide of iron and potassium. It is now shown to be really a ferricyanide, having the composition, Fe_3Cfy_2 , its production by the reaction between potassium ferrocyanide and ferric chloride, being completed only on the application of heat. It may be produced equally from a ferrous salt and potassium ferricyanide. If

soluble blue be precipitated and then washed with a solution of potassium chloride, the wash-waters will contain potassium ferricyanide, which is a proof not only that the soluble blue is a ferricyanide, but that it is formed of two distinct ferricyanides, which may be separated without destroying the compound, or affecting its solubility, and its formula ought really to be written, $2\text{Fe}_3\text{Cfy}_2 \cdot 2\text{K}_3\text{Cfy}_2$.

Various metallic salts react upon soluble blue; they do not yield the corresponding ferricyanides, but variable compounds, belonging to a totally different type. The reaction is complete only on heating, though all metallic salts precipitate the blue even in the cold.

The following salts of the series were obtained. They all resemble Prussian blue, save the zinc-salt, which is pale green, and the lead-salt, which is yellowish-white:—



Salts of mercury and silver partially decompose the soluble blue.

When washed with a weak acid, those of the above salts which contain 1 atom of iron outside the radicle, lose 1 atom of the metal joined to the iron; those which contain 2 atoms of iron, without the radicle, may lose 1 atom of metal and 1 atom of iron. The following were obtained:—



The lead salt was the only one of which the aspect changed by the treatment; it became bluish. The salts are insoluble, and yield nothing more on further treatment with acid. Their constitution may be explained (with the exception of that of the lead salt, which, from the fact that it changes colour by treatment with acid, may be mixed with oxide of iron, in which case it would be $\text{Pb}_4\text{FeCfy}_2$, and would be covered by the general rule) upon the following, which appears to be the only tangible hypothesis.

It is supposed that by the action of metallic salts upon soluble blue, a new ferrocyanogen radicle is formed, $\text{FeCfy}_2 = (\text{Fe}_3\text{C}_{12})$, and that this radicle can combine with 6 or 8 atoms of hydrogen to form the hypothetical acids, $\text{H}_6(\text{FeCfy}_2)$ and $\text{H}_8(\text{FeCfy}_2)$; the formulæ of the metallic salts then present nothing abnormal; they become $\text{Zn}_4(\text{FeCfy}_2)$; $\text{FeCd}_2(\text{FeCfy}_2)$; $\text{K}_2\text{Mn}(\text{FeCfy}_2)$; $\text{CrFe}(\text{FeCfy}_2)$, &c.

The soluble blue prepared by ammonium ferrocyanide is more stable, and more soluble than that yielded by the potassium salt; it may be dried without sensibly decomposing, and is not precipitated by alcohol. Its composition is $(\text{NH}_4)_6\text{Fe}_3\text{Cfy}_2 \cdot 9\text{H}_2\text{O}$. The ferrocyanides of the alkaline earths always yield an insoluble blue.

Prussian blue has the constant composition, Fe_4Cfy_3 , but the amount of combined water varies; the blue prepared with ferric chloride gave $8\text{H}_2\text{O}$; with ferric sulphate, $4\text{H}_2\text{O}$; with the nitrate, $9\text{H}_2\text{O}$.

Prussian blue is completely soluble in hot concentrated hydrochloric acid, and is reprecipitated unchanged on the addition of water. Efforts were made to crystallise it from the hydrochloric acid solution, but failed; both it and the soluble blue appear to be perfect colloids.

French blue, Fe_3Cfy_2 , is obtained pure by precipitating soluble blue with an excess of ferric chloride; it is stable. When treated with weak hydrochloric acid, or dissolved in the concentrated acid, and reprecipitated by water, it is converted into Prussian blue.

Ferrocyanide of Lanthanum, $\text{KLaCfy} \cdot 4\text{H}_2\text{O}$.—For general remarks, see Cerium.

Ferrocyanide of Lead, $\text{Pb}_2\text{Cfy} \cdot 3\text{H}_2\text{O}$.—It may be prepared either with yellow prussiate, or hydroferrocyanic acid. It loses all its water at 100° , and is absolutely insoluble in water, acids, or ammonia.

Ferrocyanides of Manganese.—(A.) $5\text{Mn}_2\text{Cfy} \cdot 4\text{K}_4\text{Cfy} \cdot 4\text{H}_2\text{O}$; rose-white. (B.) $\text{Mn}_2\text{Cfy} \cdot 7\text{H}_2\text{O}$; brownish-white.

(A) is prepared by precipitating yellow prussiate with a manganese salt. Its composition is constant, whichever reagent is in excess.

(B) obtained by precipitating hydroferrocyanic acid with a manganese salt.

Ferrocyanides of Molybdenum.—(A.) $\text{Mo}_3\text{Cfy} \cdot \text{K}_4\text{Cfy} \cdot 40\text{H}_2\text{O}$; very dark brown. (B.) $\text{Mo}_4\text{Cfy} \cdot 20\text{H}_2\text{O}$; paler brown. (C.) $\text{Mo}_2\text{Cfy} \cdot 8\text{H}_2\text{O}$; yellowish-brown. (D.) $\text{Mo}_2\text{Cfy} \cdot 14\text{H}_2\text{O}$; clear brown.

(A) is obtained by precipitating yellow prussiate with acidulated ammonium molybdate, which must be in great excess, since the precipitate is soluble in the yellow prussiate. The formula given by Atterberg, for the salt prepared in the same way, viz., $\text{K}_2\text{Cfy}_2(\text{MoO}_2)_3(\text{MoO}_3)_2 \cdot 20\text{H}_2\text{O}$, was derived, it is thought, from an error of calculation.

(B) is obtained by precipitating yellow prussiate by molybdenum chloride, or any salt of molybdenum.

(C) is obtained by precipitating hydroferrocyanic acid by an excess of ammonium molybdate.

(D) is obtained by precipitating the molybdate by excess of hydroferrocyanic acid. It is very soluble in water, from which alcohol precipitates it.

All these salts are but slightly stable, except (C). They are soluble in ammonia, which decomposes them, but they are reprecipitated by acids, (C) separating in the state of (D).

Ferrocyanides of Nickel.—(A.) $\text{Ni}_2\text{Cfy} \cdot \text{K}_4\text{Cfy} \cdot 6\text{H}_2\text{O}$, rose-grey. (B.) $\text{K}_2\text{Ni}_3\text{Cfy}_3 \cdot \text{K}_4\text{Cfy} \cdot 13\text{H}_2\text{O}$; clear green. (C.) $\text{Ni}_2\text{Cfy} \cdot 14\text{H}_2\text{O}$, or $11\text{H}_2\text{O}$; dark brown, or greenish-grey. (D.) $\text{Ni}_7\text{Cfy}_4 \cdot 47\text{H}_2\text{O} = 2\text{Ni}_2\text{Cfy} \cdot \text{Ni}_3\text{Cfy}_3 \cdot 47\text{H}_2\text{O}$; dirty green.

(A) and (B) are obtained with the yellow prussiate, the latter when this salt is in excess; (C) and (D) by hydroferrocyanic acid, the former with excess of nickel. (C) has $14\text{H}_2\text{O}$, when precipitated from cold solutions, and $11\text{H}_2\text{O}$, when the solutions are hot.

Ferrocyanides of Niobium.—(A.) $\text{KNb}_{16}\text{Cfy}_2 \cdot 67\text{H}_2\text{O}$. (B.) $\text{K}_2\text{Nb}_{12}\text{Cfy} \cdot 39\text{H}_2\text{O}$.

These bodies are probably mixtures of the ferrocyanides with niobic acid. Niobate of potassium is not precipitated by yellow prussiate, save in the presence of a large quantity of hydrochloric or sulphuric acid, while themselves precipitate niobic acid. Both form brown precipitates, which may be dried without decomposition. Atterberg has given the formula, $\text{Cfy}_6(\text{NbO})_5 \cdot \text{K}_3 \cdot 10\text{H}_2\text{O}$, but his figures calculate out better as $\text{K}_2\text{NbCfy} \cdot 4\text{H}_2\text{O}$, or $\text{K}_2\text{Nb}_3\text{Cfy}_3 \cdot 12\text{H}_2\text{O}$.

Silver Ferrocyanides.—(A.) $\text{Ag}_4\text{Cfy} \cdot \text{H}_2\text{O}$. (B.) $\text{Ag}_4\text{Cfy} \cdot (\text{NH}_4)_2\text{O}$.

(A) was prepared by reacting with yellow prussiate, or hydroferrocyanic acid, on excess of silver nitrate. It is white, but rapidly becomes blue in the air; should be washed with boiling water, and dried over sulphuric acid.

(B) was prepared by treating (A) with ammonia. It is white, but much less stable than (A). The ammonia was estimated in this, as in all the other ferrocyanides, by treatment with potash, and absorbing the evolved gas in a standard solution of sulphuric acid.

Tin Ferrocyanides.—(A.) $\text{Sn}_3\text{Cfy}_2 \cdot 18\frac{1}{2}\text{H}_2\text{O}$; deep grey. (B.) $\text{Sn}_2\text{Cfy} \cdot 4\text{H}_2\text{O}$; white. (C.) $\text{Sn}_3\text{Cfy}_4 \cdot 25\text{H}_2\text{O}$; bluish-white.

(A) is prepared by precipitating yellow prussiate by stannic chloride. (B) by stannous chloride.

(C) by precipitating potassium ferricyanide with stannous chloride. Stannic chloride is without action on potassium ferricyanide. These salts are rather unstable; insoluble in water and acids, slightly soluble in ammonia.

Atterberg has described a salt of the formula, $10\text{Cfy} \cdot \text{Sn} \cdot \text{K}_4\text{Cfy} \cdot 230\text{H}_2\text{O}$, but the numbers he obtained correspond equally with $\text{KSn}_3\text{Cfy}_3 \cdot 68\text{H}_2\text{O}$.

Atterberg's formula assumes tin to be tetratomic, but the salts (A) and (B) above would remain unexplained. They were prepared several times, and found to be of constant composition.

Ferrocyanides of Titanium.—(A.) $\text{K}_3\text{Ti}_3\text{Cfy}_2 \cdot 11\text{H}_2\text{O}$. (B.) $11\text{Cfy}_2 \cdot \text{Ti}_2 \cdot \text{K}_4\text{Cfy} \cdot 49\text{H}_2\text{O}$. (C.) $\text{Ti}_7\text{Cfy}_3 \cdot 25\text{H}_2\text{O}$.

They were obtained by precipitating yellow prussiate with oxychloride of titanium: (A) with an excess of the former; (B) with slight excess; and (C) with great excess of the latter. (A) is soluble in the yellow prussiate, and separates with difficulty as a gelatinous precipitate. (C) is probably a mixture of the ferrocyanide with titanous oxide or acid.

Ferrocyanides of Tungsten.—(A.) $\text{K}_2\text{W}_6\text{Cfy} \cdot 20\text{H}_2\text{O}$. (B.) $\text{KW}_2\text{Cfy} \cdot 7\text{H}_2\text{O}$.

The former is obtained with an excess of yellow prussiate, the latter with excess of ammonium tungstate. They are soluble in water, and reprecipitated by acids, and probably consist of mixtures of the ferrocyanides with tungstic acid.

Ferrocyanides of Uranium.—(A.) $3\text{U}_2\text{Cfy} \cdot \text{K}_4\text{Cfy} \cdot 12\text{H}_2\text{O}$. (B.) $\text{UCfy} \cdot 10\text{H}_2\text{O}$. Both brown.

(A) is formed by precipitating yellow prussiate with excess of uranium nitrate; (B) by precipitating it with excess of the green uranium salt. In a vacuum they dry without decomposition.

Ferrocyanides of Vanadium. $\text{K}_3\text{V}_3\text{Cfy}_2$.—The vanadates and the salts of vanadium oxide precipitate the yellow prussiate, the precipitates being clear green, very bulky, and somewhat soluble in water. The formula is regarded by the author as doubtful on account of the difficulty of obtaining an exact estimation of vanadium.

Ferrocyanide of Yttrium. $\text{KYCfy} \cdot 2\text{H}_2\text{O}$.—A white powder prepared with yellow prussiate and yttrium nitrate. It has been described by Clève and Hoeglund. (See Erbium.)

Ferrocyanides of Zinc.—(A.) $3\text{Zn}_2\text{Cfy} \cdot \text{K}_4\text{Cfy} \cdot 12\text{H}_2\text{O}$. (B.) Zn_2Cfy_2 .

$4\text{H}_2\text{O}$. Both white, and absolutely insoluble in water. (A) was prepared from yellow prussiate and any salt of zinc; (B) with hydroferrocyanic acid and any salt of zinc, regardless of proportions in either case. (B) may also be formed by treating zinc ferricyanide with ammonia.

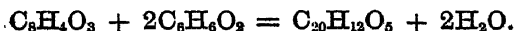
The salts of mercury, chromium, gold, and platinum, and acetate of iron modified by heat, do not precipitate the yellow prussiate.

C. H. P.

Pseudosulphocyanogen (CNSH). By W. R. H. (*Chem. News*, xxxiv, 80).—By treating sulphocyanates, more especially the alkaline salts, with chlorine, bromine, or iodine, a yellow body insoluble in water is produced, which was supposed to be the radicle *sulphocyanogen*, but was found on analysis to contain a small and somewhat variable amount of hydrogen not removable by excess of chlorine: hence it was called *pseudosulphocyanogen*. From some experiments made to obtain this substance in the pure state, it appears that the hydrogen is not the only element which varies in its amount in differently prepared specimens. Considerable differences in the composition of the product are obtained with slight variations of temperature and strength of the sulphocyanate solutions. NH_4SCy solution absorbs chlorine rapidly, with rise of temperature. When the vessel is kept cool ($10\text{--}15^\circ\text{C}$.) and the chlorine not used in excess, a light yellow precipitate is produced, which, after washing with hot water, in which it is slightly soluble, appears to undergo a decomposition. A considerable amount of hydrocyanic acid is given off from the substance, when suspended in the solution which has been submitted to the action of chlorine. No hydrocyanic acid is given off after washing and drying at 100° . Pseudosulphocyanogen may possibly be utilised as a water or oil colour; it may be obtained of several yellow shades, and is exceedingly permanent. It is not altered by the action of light, or when ground up moist with nitrate of lead, bismuth, or silver, or with silver sulphide. It requires high temperatures for its decomposition. When it is mixed wet with solid silver nitrite and exposed to sunlight, a blackening occurs, due only to intermixed reduced silver. From analysis the formula CNHS was obtained, but the tripled formula $\text{C}_3\text{H}_3\text{N}_3\text{S}_3$ agrees better with the product of its decomposition by heat, viz., mellone.

D. B.

The Compounds of Pthalic Acid with the Phenols. Part I. By A. BAEYER (*Liebig's Annalen*, clxxxiii, 1—74).—(1.) *Fluorescein*. This compound is obtained by heating a mixture of 5 parts of phthalic anhydride and 7 parts of resorcin to $195\text{--}200^\circ$ until a solid mass is formed:—



The residue is boiled with water and the undissolved portion washed with alcohol, which dissolves resinous bye-products. The crude fluorescein is dissolved in dilute soda, precipitated with dilute sulphuric acid, and extracted with ether. On adding a little absolute

alcohol to this solution and distilling off the ether, fluorescein crystallises in grains or crusts. The crude fluorescein may also be purified by boiling it with a quantity of dilute soda which is insufficient to dissolve the whole, or by adding calcium chloride to its alkaline solution, filtering off the dark brown precipitate, and adding sodium phosphate, which produces a brown precipitate of calcium phosphate. The liquid is then again filtered and the pure compound precipitated from the filtrate by an acid.

Fluorescein is an amorphous, yellow, flocculent precipitate, which, on standing, heating, or drying, becomes crystalline, and consists of $C_{20}H_{12}O_6 + H_2O$. From alcohol it crystallises in dark red anhydrous grains, and from wood-spirit in yellow prisms, which probably contain methyl alcohol. It is almost insoluble in cold water, and dissolves sparingly in hot water with a yellow colour; in presence of acids it is more freely soluble. When freshly precipitated it dissolves readily in alcohol, ether, &c., but in the crystallised state only slowly, and after continued boiling. In hot acetic acid it is readily soluble, but nearly insoluble in benzene, toluene, and chloroform. The ethereal solution is pale yellow, and not fluorescent, while the yellowish-red alcoholic solution shows a green fluorescence. It may be heated to 280° without any change, and begins to decompose at 290° .

Fluorescein dyes silk and wool yellow, but does not combine with mordants.

Fluorescein is a very weak acid, dissolving in strong alkalis with a dark red colour. This solution is not fluorescent, but changes on dilution to yellowish-red and yellow, and then exhibits a splendid yellowish-green fluorescence like that of uranium glass, and even if so much water is added that the liquid appears colourless in transmitted light, it shows in reflected light a green tinge like the colour of some Alpine lakes. The concentrated solution allows only the red and yellow rays to pass, while when dilute it gives an absorption-spectrum with a broad dark band in the green.

When alcoholic ammonia is added to a solution of fluorescein in ether, a reddish-yellow precipitate is formed, which loses ammonia on boiling or drying. In lime- and baryta-water fluorescein dissolves with a reddish-yellow colour; its alkaline solution is not precipitated by magnesium salts, while alum produces a reddish-yellow precipitate, which, on further addition of alum, becomes yellow, and then consists of pure fluorescein. The salts of some other heavy metals behave in a similar way; the lead and silver salts are more stable, and form reddish precipitates.

The striking colouring properties of fluorescein afford the means of detecting even traces of resorcin in presence of other phenols. It is only necessary to heat the substance with an excess of phthalic anhydride to near the boiling point of the latter. If the melt remains colourless, neither resorcin, nor pyrogallol or phloroglucin is present, but if it has a yellowish-red colour, these substances may be present. In the latter case the residue is dissolved in dilute soda, the smallest trace of resorcin then becoming apparent by the fluorescence of the solution, while pyrogallol yields a blue, and phloroglucin a yellow liquid, which are not fluorescent. If a large proportion of pyrogallol

should interfere with the reaction, a solution of potassium permanganate is carefully added, which destroys the gallein at once, but acts only slowly on the fluorescein.

Diacetyl-fluorescein, $C_{20}H_{10}O_5(C_2H_3O)_2$, is formed by heating fluorescein with four or five times its weight of acetic anhydride to 140° , until, on mixing a small quantity with alcohol, yellow crystals separate out, which are insoluble in ammonia. The whole is now treated in the same way, in order to convert the anhydride into the acetic ether. The crystals are dissolved in acetic acid, and the solution poured into several volumes of alcohol, when the pure compound crystallises in colourless needles melting at 200° . It dissolves but sparingly in alcohol and wood spirit, but readily in acetic acid and hot acetone, while it is insoluble in ether, benzene, and chloroform. It is decomposed into fluorescein and acetic acid by boiling alkalis, and rapidly in alcoholic solution; the same decomposition is produced by concentrated sulphuric acid and hot hydrochloric acid.

Dibenzoyl-fluorescein, $C_{20}H_{10}O_5(C_7H_5O)_2$, is obtained by heating fluorescein with benzoyl chloride for an hour to 140° . The dark brown residue is boiled with water and crystallised from acetone. It forms colourless crystals melting at 215° , dissolves sparingly in alcohol, wood-spirit, and ether, but readily in hot acetone. Alcoholic potash and concentrated sulphuric acid resolve it into its components.

Monethyl-fluorescein, $C_{20}H_{11}O_5(C_2H_5)_2$.—To prepare this compound, potash-solution is saturated with fluorescein, the liquid evaporated to dryness, and the residue heated for 2—3 hours to 120° with more than 2 mol. of ethyl bromide and ten times its weight of alcohol. The solution thus obtained is diluted with water and treated with sodium carbonate to remove unaltered fluorescein. The monethyl-compound is then extracted with ether, the solution evaporated, the residue dissolved in alcohol, and the solution concentrated. On heating the syrupy residue with ether, monethyl-fluorescein crystallises in pale yellow needles melting at 155 — 156° . It is readily soluble in alcohol, wood-spirit, chloroform, and benzene, and separates from these solvents as a syrupy mass, miscible with ether, and crystallising therefrom in needles, which are but sparingly soluble in the pure solvent. When water is added to a hot alcoholic solution, it becomes milky on cooling, and deposits turbid, yellow crystals. The compound is insoluble in dilute alkalis, which on heating decompose it. Concentrated sulphuric acid dissolves the ether with a greenish-yellow colour and a light green fluorescence, which disappears on adding water; on neutralising this solution the unaltered compound is precipitated.

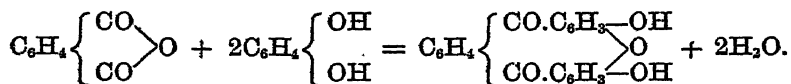
Diethyl-fluorescein, $C_{20}H_{12}O_5(C_2H_5)_2$, is not formed by the action of ethyl bromide on the potassium-compound, and only sparingly when the silver-compound is heated with ethyl bromide and ten times its quantity of alcohol. The reddish-brown solution thus formed is concentrated and precipitated with water, the precipitate is treated with sodium carbonate to dissolve unaltered fluorescein, and the insoluble portion dissolved in ether, which is then evaporated, and the residue crystallised from alcohol, from which it separates in pale yellow plates. The compound is sparingly soluble in ether and alcohol; the alcoholic solution shows a vivid yellow fluorescence. It is not changed by dilute

alkalis, but concentrated solutions and sulphuric acid decompose it into alcohol and fluorescein.

Fluorescein chloride, $C_{20}H_{10}O_3Cl_2$, is easily obtained by heating one mol. of fluorescein with two mols. of phosphorus pentachloride for 1—2 hours to 100° . The product is successively treated with boiling water, a warm solution of sodium carbonate, and boiling alcohol. On dissolving the residue in hot toluene, and adding alcohol, the chloride crystallises out, and is purified by repeating this operation. It forms colourless prisms melting at 252° , and dissolving readily in hot benzene, toluene, and chloroform, and sparingly in alcohol, ether, acetic acid and chloroform. It is not changed by aqueous or alcoholic potash, while on fusing it with potash it is completely destroyed; but on heating it with slaked lime and a little water to 230° for some hours, it is again converted into fluorescein. Cold concentrated sulphuric acid dissolves it without alteration, but on boiling the solution, decomposition takes place, and on adding water, dark red flakes are precipitated, dissolving in ether with a wine-red colour.

When the chloride is heated with an excess of fuming hydriodic acid to 150° for 5—6 hours, the compound $C_{20}H_{12}O_3Cl_2$ is formed, crystallising from alcohol, ether, and acetic acid in small, rhombohedral plates, melting at 229 — 230° . It dissolves in dilute, but not in concentrated, alkalis, and contains, probably, in the place of the two carbonyl groups, CO, the groups CH.OH.

The foregoing results prove that fluorescein contains two hydroxyls, and its constitution and formation are explained by the following equation:—



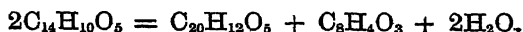
It is, therefore the anhydride of resorcin-phthalein,—



The latter compound appears to be formed by the action of strong alkalis on fluorescein, for on boiling the latter with an excess of soda, the liquid, when sufficiently concentrated, becomes dark violet, and crystals of the same colour separate out. On adding water, the solution first becomes red, then assumes a dingy colour, and on standing, or more quickly on heating, it assumes the colour of an alkaline solution of fluorescein, which is precipitated on adding an acid. When alcohol is added to the violet solution, it becomes intensely violet, and then gives an absorption-spectrum having a dark band between the blue and green, and another between the green and red. If an acid be added to the violet alkaline solution, a yellow precipitate is formed, dissolving in ether with a yellow colour, and on then adding an alkali the latter becomes again violet. These reactions show that resorcin-phthalein is a stable body in presence of acids or strong alkalis, but that in a weak alkaline solution it soon changes again into its anhydride.

When fluorescein is boiled down with an excess of caustic soda, the violet colour changes into a brownish-yellow. On dissolving the melt in water, and adding an acid, a milky liquid is formed, from which

crystals soon separate. They were purified by crystallisation from dilute alcohol, and in this manner large yellowish striated crystals were obtained, having the formula $C_{14}H_{10}O_5 + H_2O$, and losing their water at 100° . They melt at about 200° , but decompose even below this temperature when heated for some time. They dissolve sparingly in hot water, very freely in alcohol and ether, and form with alkalis a yellow solution, which gives with silver nitrate a yellowish-white precipitate; on heating it, metallic silver is formed. When the substance is heated with resorcin, it yields fluorescein, which is also formed by heating the substance alone, phthalic anhydride subliming at the same time—



These reactions show that the body is *monoresorcin-phthalein*,
 $C_8H_4 \begin{cases} CO.C_6H_3(OH)_2 \\ CO.OH \end{cases}$ On heating it more strongly with soda, it is resolved into resorcin and phthalic acid, which is further decomposed into carbon dioxide and benzoic acid.

When fluorescein is heated with soda-lye and zinc-dust, the solution becomes colourless. On adding an acid and shaking with ether, *fluorescin* is dissolved, and remains on evaporation as a colourless varnish. It forms an alkaline, colourless solution, which absorbs oxygen, while oxidising agents convert it quickly into fluorescein.

Fluorescein dissolves in concentrated sulphuric acid, with a dark red colour, a compound of the two bodies being formed, which is obtained pure by heating 2 mols. of resorcin and one of phthalic anhydride with an equal weight of sulphuric acid to 100° for 5–6 hours. The melt is washed with cold water and crystallised from wood-spirit at a low temperature. In this manner yellowish-red prisms are obtained, having the empirical formula $C_{20}H_{12}O_5 + SO_3$, and melting at 140 – 150° . They are decomposed by recrystallisation, become turbid in damp air, and are resolved by warm water or alkalis into their components.

When fluorescein is boiled with sulphuric acid for some time, *resorcin-coerulein* is formed, which is precipitated by water in dark red flakes. It dissolves in alkalis with a greenish-blue, and in ether with a reddish-violet colour, and is also soluble in water, the concentrated solution being red, and the dilute splendid reddish-violet. It is reduced in an alkaline solution by zinc-dust, and the red liquid thus formed again becomes blue on exposure to the air.

Dinitro-fluorescein, $C_{20}H_{10}(NO_2)_2O_5$, is obtained, but not quite pure, by dissolving fluorescein in 20 parts of sulphuric acid, and adding to the solution at 0° two parts of fuming nitric acid. It is an amorphous yellow powder, dissolving in potash with a brown colour, which on heating changes to red and blue. On heating it with acetic anhydride, the compound $C_{20}H_8(NO_2)_2O_5(OCOCH_3)_2$ is formed, crystallising from alcohol in pale yellow needles. The same compound is formed by acting with nitric acid on a solution of acetylfluorescein in sulphuric acid, but not by dissolving it in cold nitric acid, while, on heating, tetranitrofluorescein is formed.

When dinitrofluorescein, or better, its acetyl-compound, is boiled for

five minutes with 20 times its weight of a lye containing 15 per cent. of alkali, the liquid changes to red and then blue. Acids produce a yellow precipitate, crystallising from ether-alcohol in glistening red crystals, consisting of $C_{20}H_{12}(NO_2)_2O_6$. This compound dissolves in alkalis with a blue colour, which on dilution first changes into violet and then again into blue. In its absorption-spectrum the yellow is completely cut off, and it shows a faint band between the blue and green. The potassium salt of this *dinitro-fluorescein hydrate* appears to be formed by acting with alcoholic potash on dinitro-fluorescein, a blue crystalline body separating out, which is soluble in water.

Hydrochloric acid and tin reduce dinitro-fluorescein in an alcoholic solution, diamido-fluorescein being probably formed. Its hydrochloride crystallises in greenish-grey needles, and dissolves in alkalis with a cherry-red colour. With nitrous acid it yields a body crystallising in yellow needles, and dissolving in alkalis with a light reddish-brown colour, and a strong dark green fluorescence.

Tetranitro-fluorescein, $C_{20}H_8(NO_2)_4O_6$, is formed by adding an excess of fuming nitric acid to about 5 grams of fluorescein; a violent reaction soon sets in, and after all is dissolved, the compound is precipitated with water, washed with water and a little alcohol, and dissolved in 50 parts of boiling glacial acetic acid. On cooling, the compound separates in colourless, warty crystals. It is sparingly soluble in alcohol, with a yellowish-red colour, and a faint yellowish-green fluorescence. The addition of a little mineral acid changes the colour into a pale reddish-violet, while on adding more, the liquid becomes colourless. In alkalis it dissolves with a yellowish-red colour, and in boiling water with a red colour. It dyes on wool an intense and fast orange. Dilute boiling alkalis do not change it, but concentrated alkalis change the colour to brown, and then to a pale yellow.

Tin and hydrochloric acid reduce tetranitrofluorescein to an amido-compound, dissolving in alkalis with a splendid bluish-violet colour. In ammonium sulphide it dissolves with a brownish-red colour, which changes to violet on heating. Acids produce a brown precipitate, crystallising from ether in brown needles, and dyeing on silk a dingy violet.

Monobromofluorescein is formed by suspending fluorescein in 4 parts of glacial acetic acid, and adding the required quantity of bromine mixed with 4 parts of acetic acid. The compound is a yellowish-red amorphous body, which could not be obtained in crystals, and is changed by boiling acetic anhydride into a sticky mass. The alkaline solution has a reddish colour and faint green fluorescence.

Dibromofluorescein is formed by using 2 mol. of bromine. It forms compact reddish-brown needles, with a deep green reflection, melting at 260—270°, and dissolving sparingly in acetic acid, alcohol, and acetic ether. Its alkaline solution is reddish-yellow, and shows a faint yellowish-green fluorescence. On boiling, the liquid changes into violet and blue, and the fluorescence into a dark green. On boiling it with acetic anhydride, the diacetyl-compound is formed, crystallising in colourless needles, which become red at 180°, and melt at 208—210°.

Tetrabromofluorescein or *Eosin*, $C_{20}H_6Br_4O_6$.—This beautiful body,

which is now manufactured on the large scale, and has been introduced into commerce by H. Caro as a dye-stuff, is formed by mixing fluorescein with 4 parts of acetic acid, and adding the required quantity of bromine, which is diluted with four times its weight of acetic acid. It is also formed by adding bromine to a mixture of fluorescein and alcohol. It is purified by converting it into the pure potassium salt, and decomposing it by a mineral acid. An amorphous reddish-yellow precipitate is thus obtained, which is dried and dissolved in twenty times its weight of absolute alcohol, which is then distilled off until crystals begin to separate; or the potassium salt is decomposed by dilute sulphuric acid, and the liquid shaken with ether. The amorphous eosin is much more freely soluble than the crystals; the alcoholic solution is reddish-yellow and not fluorescent; it is but sparingly soluble in acetic acid, and almost insoluble in water, chloroform, and benzene. The crystals obtained from alcohol consist of $C_{20}H_8Br_4O_6 + C_2H_5O$, the alcohol being given off at 100° . If to a boiling alcoholic solution water is added until it becomes turbid, and then a little hydrochloric acid, the liquid on boiling becomes clear again, and dull flesh-coloured crystals separate out, consisting of the pure compound.

Eosin is a bibasic acid; its salts are decomposed by mineral acids, but only imperfectly by acetic acid.

The *potassium salt*, $C_{20}H_8Br_4O_6K_2 + 6H_2O$, occurs in commerce as "soluble eosin," and forms brown, indistinct, prismatic crystals, with a blue and yellowish-green reflection. To obtain it in well-defined crystals, 100 parts are dissolved in 50 parts of water, and after addition of 100 parts of alcohol and filtering, the solution deposits on standing splendid large plates, which in transmitted light appear red, and show the above reflection. They form a red powder, and belong to the triclinic system, being combinations of ∞P , $\infty \bar{P} \infty$, $\infty \bar{P} \infty$. They contain 5 mol. of water. On dissolving them in dilute alcohol, small reddish-brown crystals with a greenish-yellow reflection crystallise on cooling, which appear to contain 1 mol. of alcohol. When the aqueous solution is quickly dried, the salt separates as a varnish having a yellowish-green metallic lustre. It dissolves in 2 parts of water. The concentrated solution is dark, yellowish-red, and in a thin layer pale pink. A dilute solution is yellowish-red, and exhibits a strong greenish-yellow fluorescence, which is also seen when the solution is very weak. Its absorption-spectrum has a broad dark band in the green. Its alcoholic solution exhibits similar colours, but a stronger fluorescence. The absorption-spectrum is destroyed by mineral acids, but not by acetic acid. A dilute aqueous solution containing 1 part in 150 gives the following reactions:—

It is not changed by magnesium sulphate. Calcium and barium chloride give crystals on quickly boiling down the liquid, while cadmium sulphate deposits crystals in 12 hours, and nickel sulphate after weeks. Mercuric chloride gives at once a crystalline precipitate, and on standing a mixture of red and yellow crystals. Red amorphous precipitates are formed by salts of silver and lead, and reddish-brown by copper salts, while alum, zinc sulphate, stannous chloride, cobalt, nitrate, ferric and ferrous chloride, manganese sulphate, and bismuth nitrate, give amorphous reddish-yellow precipitates.

The *ammonium salt*, $C_{20}H_5Br_4O_5(NH_4)_3$, is obtained in small, red needles, when a solution of tetrabromofluorescein in alcoholic ammonia is concentrated; they give off some ammonia on drying.

The *barium salt*, $C_{20}H_5Br_4O_5Ba + 2H_2O$, is prepared by mixing a solution of 2 parts of the potassium salt with a solution of 1 part of barium chloride in such a proportion that 60 parts of water are present. On boiling, crystals separate out, of which more are obtained on evaporating the mother-liquor after cooling; they form small rhombic plates with a green reflection; the aqueous solution is yellowish-red, and shows a green fluorescence.

The *cupric salt*, $C_{20}H_5Br_4O_5Ca + \frac{1}{2}H_2O$, forms small yellowish-red needles, with a faint green lustre; it is more freely soluble than the barium salt.

The *cadmium salt* is deposited from a dilute solution in very glistening, small six-sided plates, having a brilliant greenish-yellow lustre; at 100° it loses water and becomes green.

The *silver salt*, $C_{20}H_5Br_4O_5Ag_3$, is a dark red precipitate, which is insoluble in salt-solutions, but dissolves in pure water and alcohol, and on heating it with the latter to 150° and leaving the solution to cool, it crystallises in microscopic, indistinct prisms, which are almost black. The precipitated salt becomes green when dried in a vacuum.

The *lead salt*, $C_{20}H_5Br_4O_5(PbOH)_2$, is obtained as a red precipitate, when the potassium salt is mixed with lead acetate, while the nitrate produces a similar precipitate which is not quite pure $C_{20}H_5Br_4O_5Pb$.

Red Monethyl-tetrabromofluorescein or *Erythrin*, $C_{20}H_5Br_4O_3 \left\{ \begin{array}{l} OC_2H_5 \\ OH \end{array} \right.$, is formed when the potassium salt of eosin is heated to 140 — 150° for 4—5 hours with 15 parts of alcohol and a quantity of potassium ethylsulphate, which would be sufficient to form the neutral ether. On cooling, the tubes contain a gelatinous mass mixed with large crystals, which, on adding water, remain undissolved, while the unchanged potassium salt of erythrin dissolves. The crystals, which consist of the potassium-compound of eosin, are dissolved in alcohol of 50 per cent., and the solution mixed with acetic acid. If it be concentrated, erythrin separates as an amorphous precipitate, but from a dilute solution, it crystallises on evaporation in red needles with a beetle-green lustre. Erythrin is also formed, but not so readily, by the action of ethyl bromide on the potassium salt of eosin.

Erythrin dissolves slowly but freely in alcohol, with a reddish-yellow colour, and more readily in chloroform and acetic acid. From the first two solvents it separates in warty crystals, but when its solution in a mixture of acetic acid and alcohol is diluted with water, distinct crystals are obtained. When erythrin is heated with sulphuric acid to 150° , it is again converted into eosin.

The *potassium salt*, $C_6H_7Br_4O_5(C_2H_5)K + H_2O$, is very sparingly soluble in water and absolute alcohol, but readily in hot, dilute alcohol of 50 per cent. The concentrated solution is yellowish-red, the dilute, pale pink, with a yellowish-green fluorescence; its absorption-spectrum is almost the same as that of eosin. The salt, called in commerce, "insoluble eosin," dyes silk and wool like eosin, but the shades are more inclined to violet. The crystals appear to be rhombohedrons.

They have a strong beetle-green lustre, and yield a pink powder. Silver nitrate precipitates the solution; the precipitate is amorphous, red in reflected light, and beautiful violet in transmitted light; on heating or standing it becomes crystalline, and in the dry state it has a beetle-green lustre, and appears in transmitted light intensely blue. The lead salt is a similar precipitate.

Colourless Monethyl-tetrabromofluorescein.—This isomeride of erythrin is formed, together with the diethyl-compound, when the silver salt of eosin is heated with an excess of ethyl iodide or bromide, and twenty times its weight of alcohol to 100° for 3–4 hours. To separate the two ethers, the product is repeatedly exhausted with boiling alcohol, in which the monethyl-ether is more readily soluble and crystallises on cooling in yellow needles. As soon as the red crystals of the diethyl-ether appear, the treatment with alcohol is stopped, and the yellow crystals boiled with a solution of potash in alcohol of 50 per cent., which dissolves chiefly the monethyl-compound. The solution is then mixed with more dilute alcohol and acetic acid, and the ether which separates out is again treated in the same way, and is thus obtained in colourless needles. It is sparingly soluble in boiling alcohol, and a little more freely in glacial acetic acid; its very pale solution is coloured light yellow by alkalis, and gives yellowish-white precipitates with silver nitrate and lead acetate. It dissolves but sparingly in carbonates and dilute alkalis.

The existence of two isomeric monethyl-compounds shows that the two hydroxyls occupy different positions.

Diethyl-tetrabromofluorescein, $C_{26}H_8Br_4O_5(C_2H_5)_2$, is obtained not only as described above, but also by heating the silver salt of the red monethyl-ether with ethyl iodide. To isolate it from the residue from the preparation of the white monethyl-ether, this residue is exhausted with chloroform, and the crystals, after boiling with dilute alcoholic potash, are recrystallised from chloroform. It forms small but well-defined crystals, which appear to be rhombohedrons, and dissolve very sparingly in alcohol and ether, with a yellowish colour, and freely in chloroform and glacial acetic acid, with a reddish-yellow colour. Aqueous alkalis do not decompose it on boiling, but alcoholic potash, as well as hot sulphuric acid, converts it into eosin.

Monomethyl-tetrabromofluorescein or *Methylerythrin*, $C_{20}H_7Br_4O_5(CH_3)$, is sparingly soluble in alcohol, more freely in chloroform, it crystallises in red needles, having a beetle-green lustre.

Acetyl-tetrabromofluorescein is formed by heating eosin with three times its weight of acetic anhydride to 140° . It forms colourless needles dissolving sparingly in alcohol, acetone, wood-spirit, and acetic ether, and more freely in hot benzene and chloroform. On heating, it becomes red at 180° , but melts only at 278° .

Tetrabromofluorescein chloride, $C_{20}H_4Br_4O_5Cl_2$, is obtained by heating tetrabromofluorescein with phosphorus pentachloride for an hour to 100° . The product, after being well boiled with water and a dilute alkali, is dissolved in seventy times its weight of concentrated sulphuric acid at 150° , filtered through asbestos, and then mixed with 3 volumes of alcohol. The liquid is then heated to the boiling point, and water added, until crystals begin to separate out. It forms colour-

less needles, which melt and sublime without decomposition; its only solvent is concentrated sulphuric acid, which decomposes it only at the boiling point.

When tetrabromofluorescein is heated with concentrated potash on a water-bath, the liquid soon assumes a blue colour, and shows, when diluted, a very strong, dark-green fluorescence. The dilute solution turns red in contact with the air, but the concentrated remains blue. Mineral acids produce a pale reddish-yellow precipitate of the hydrate $C_{20}H_3Br_4O_5 + H_2O$, which has undoubtedly a constitution analogous to that of the dinitro-compound.

When the solution is heated on a water-bath, the blue solution changes into dark yellow. This change takes place more quickly if the potassium-salt is heated with twenty times its weight of soda of 50 per cent. Mineral acids precipitate from the solution—

Dibromomonoresorcin-phthalein, $C_6H_4 \left\{ \begin{array}{l} CO.C_6HBr_2(OH)_2 \\ CO_2H \end{array} \right.$, crystal-

lising in small, colourless, rhombic plates, which melt at $218-220^\circ$. It is almost insoluble in water, and dissolves in alkalis and alcohol, with a yellow colour. On fusing it with resorcin, dibromofluorescein seems to be formed, and when it is heated with phenol and sulphuric acid to 120° , a body is formed dissolving in alkalis with a red colour.

The acid liquid from which the preceding compound has been precipitated, contains *dibromoresorcin*, $C_6H_2Br_2(OH)_2$, which is shaken out with ether. It crystallises from warm water in colourless needles, melting at $92-93^\circ$; the aqueous solution gives, with ferric chloride, first a violet colour, which soon changes into an indistinct dirty green.

Water and sodium-amalgam or zinc-dust and soda, reduce tetrabromofluorescein to fluorescein, and when the tetrabromo-compound is boiled for five minutes with twenty times its weight of concentrated sulphuric acid, *heptabromocœrulein*, $C_{46}H_{13}Br_7O_{10}$, is formed, which, by adding water, is precipitated as a dark violet mass, and during washing, begins to dissolve with a blue colour. On dissolving it in dilute potash, and adding alcoholic potash, a dark-blue precipitate of the potassium-salt is obtained, which yields, with acids, the pure cœrulein, readily soluble in acetone, from which it crystallises in steel-blue needles. The absorption-spectrum of the dilute solution shows a faint broad band in the green, and the dilute alkaline solution, which has a greenish-blue colour, gives an absorption-band in the red.

Dibromodinitrofluorescein, $C_{20}H_6Br_2(NO_2)_2O_6$, is formed by the action of nitric acid on dibromofluorescein, and by treating dinitrofluorescein with bromine. It is also obtained by dissolving 1 mol. of the tetra-nitro-compound in boiling acetic acid, and adding 2 mols. of bromine. It crystallises in compact yellow needles, which are very sparingly soluble in alcohol and acetic acid, and dissolve in alkalis with a yellowish-red colour, becoming pale pink on the addition of much water. It is not fluorescent, but gives an absorption-spectrum resembling that of eosin. The acetyl-compound forms colourless needles melting at 250° , but changing to violet at 210° .

Some of the derivatives of fluorescein have already been described by Fischer (this Journal, 1875, p. 159).

II. *Orcin-phthalein*, by E. Fischer.—This homologue of fluorescein is formed by heating phthalic anhydride with orcin, and is best obtained by heating 3 parts of phthalic anhydride, 5 parts of distilled orcin, with 5 parts of sulphuric acid for two hours to 135° ; if the temperature be kept at 100 – 120° , bye-products are formed and sulphur-dioxide is evolved. The brown melt is washed with water, dissolved in dilute potash, boiled, and then the phthalein is precipitated by acetic acid. It is purified by crystallising from acetone, and is thus obtained in groups of needles. It is insoluble in water, ether, benzene, and toluene, and readily soluble in alcohol, wood-spirit, acetone, and acetic acid. In alkalis it dissolves with an intense dark-red colour, without fluorescence when pure. With mineral acids it forms red compounds, which are soluble in water; on heating it with sulphuric acid, a coerulein is formed, which, after drying, is almost black, and dissolves in ammonia with a dark-red colour.

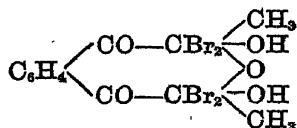
Diacetylorcin-phthalein crystallises from alcohol in silky needles having a faint bluish lustre, and melting at 219 – 220° .

Orcin-phthalein crystallises from hot acetic acid in short prisms, which, when heated with the acid for some time, become yellowish-red, *monacetyl-orcin-phthalein* being formed, which is obtained pure by heating the substances to 150° .

When orcin-phthalein is heated with hydrochloric acid and alcohol, the compound, $C_{22}H_{16}O_5 + HCl$, is formed, which, on evaporating the alcohol, separates in dark red flakes. On heating it or boiling it with water, it loses the acid, but it dissolves in alcohol, wood-spirit, and acetone without decomposition.

Tetrabromorcin-phthalein, $C_{22}H_{12}Br_4O_5$, is obtained by adding bromine to a boiling solution of the phthalein in acetic acid. It is a pale yellow crystalline powder nearly insoluble in most solvents, but somewhat more soluble in a mixture of acetone and carbon sulphide. Its almost black alkaline solution becomes dark-brown on dilution, and shows a blackish-green fluorescence.

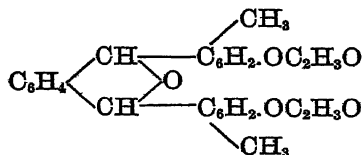
As the formation of phthalic acid from tetranitrofluorescein shows that the substitution has taken place in the resorcin-residues, it appears most likely that the same is the case with tetrabromorcin-phthalein, which is not decomposed by boiling alkalis, and must, therefore, have the following constitution:—



When the phthalein is brominated in presence of alcohol, *penta-bromorcin-phthalein* is formed, which can be distinguished from the tetra-compound only by analysis.

Orcinophthalin is obtained by heating the phthalein with dilute soda and zinc-dust; potash acts but slowly, and with difficulty. On adding dilute sulphuric acid to the colourless solution, white flakes are formed, which, when pure, do not absorb oxygen. The dry compound can be boiled with hydrochloric acid without change, but if the acid be added

to the boiling alkaline solution, the red compound of the acid with the phthalein is formed. The phthalein is sparingly soluble in water, but readily in most other solvents, and does not crystallise. The *diacetyl-compound* $C_{22}H_{16}O_4(C_2H_3O)_2$ forms small cubical crystals, melting at 211° . The constitution of this body is probably:



C. S.

Terephthalic Aldehyde. By E. GRIMAUZ (*Compt. rend.*, lxxxiii., 825—827).—The only three dialdehydes known are glyoxal, succinic aldehyde, and phthalic aldehyde. The author has prepared terephthalic aldehyde by a method discovered by himself and Lauth, viz., by oxidising the chloride of the acid radicle with dilute nitric acid or with lead nitrate. The tolylene chloride was boiled with 20 parts of water and some lead nitrate till red fumes no longer appeared. The liquid was then distilled after addition of water, and the aldehyde was carried over by the water-vapour. It has the formula $C_8H_6O_2$; it forms delicate white needles, and melts at 114 — 115° . It dissolves in ether and in alcohol, sparingly in cold water, and in about 60 times its weight of boiling water. It forms a compound with sodium disulphide, which cannot be separated from its solution. When treated with potassium cyanide it appears to be polymerised, forming a reddish-brown substance, yellow and amorphous when dry, insoluble in water and in ether, soluble in boiling alcohol and in alkalis, but not in their carbonates, and melting at 170 — 174° . It is analogous to benzoïn. The aldehyde was proved to be terephthalic by oxidation. The mixture of chlorides from which the tolylene chloride had been separated by freezing was oxidisable with difficulty with lead nitrate; the product of the oxidation appeared to be isophthalic aldehyde. It melted at 88° .

W. R.

α -Cresylsulphuric Acid. By E. BAUMANN (*Deut. Chem. Ges. Ber.*, ix., 1389—1392).—Horses' urine contains, besides phenyl-sulphuric acid, also a cresylsulphuric acid, forming a potassium salt which is less soluble in water and alcohol than the phenyl-sulphate. It is not coloured by ferric chloride, but on heating it to 150 — 160° , it seems to be changed into a cresolsulphonate, which is coloured blue by the ferric salt. The corresponding cresol (*Städeler's* taurylic acid) is identical with Engelhardt's and Latschinoff's α -cresol. It yields with bromine an unstable substitution-product, or a mixture of such.

C. S.

New Mode of Formation of Azobenzene. By R. ANSCHÜTZ and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, ix., 1398—1408).—Glaser found that by the action of sodium on parabromaniline, benzidine is formed. On repeating this experiment, the principal product was found to consist of azobenzene, no benzidine being formed.

C. S.

Haloid-Derivatives of the Nitrotoluenes. By C. WACHENDORFF (*Deut. Chem. Ges. Ber.*, ix, 1345—1347).—When the different nitrotoluenes are treated with chlorine or bromine above 100°, the substitution takes place in the side-chain. Thus, on heating paranitrotoluene with bromine to 125—130°, *paranitrobenzyl bromide* is formed, crystallising from hot alcohol in silky needles, and from cold alcohol in thin plates, melting at 99—100°. It produces a burning pain on the skin, and violently attacks the eyes and mucous membranes of the nose. By using more bromine, *paranitrobenzylene dibromide* is obtained, crystallising from hot alcohol in needles or plates melting at 82—82.5°.

When chlorine is passed into paranitrotoluene at 185—190°, *paranitrobenzyl chloride* is formed, which has already been described by Beilstein and Geitner, and by Grimaux. A more highly-substituted product could not be obtained, and if nitrotoluene is treated with antimony perchloride, *metachloro-paranitrotoluene* is formed, crystallising from hot alcohol in long, glistening, pointed prisms, melting at 64—65°. It is freely soluble in alcohol, ether, and glacial acetic acid, and sparingly in hot water, from which it crystallises in small needles. On oxidation, it yields Hübner's nitrometachlorobenzoic acid.

By acting with bromine on metanitrotoluene, *metanitrobenzyl bromide* is formed, crystallising from hot alcohol in small needles or plates, melting at 57—58°, and by using more bromine, *metanitrobenzylene dibromide* is obtained in microscopic needles melting at 101—102°.

The author formerly described the corresponding ortho-compounds; but the orthonitro-toluene which he then used contained the para-compound. Perfectly pure orthonitrotoluene yields only *dibromorthonitrotoluene*, which separates in compact plates. On recrystallisation from hot alcohol, they change into small white needles, melting at 225—226°. It is readily soluble in aqueous alkalis, and reprecipitated by acids in flakes. C. S.

Two New Modifications of Dichloronaphthalene. By P. T. CLÈVE (*Bull. Soc. Chim.* [2], xxii, 244—245).—The following table gives a view of all the dichloronaphthalenes rediscovered since Laurent's time.

Name.	Melting point.	Discoverer.
α	35—36°	Faust and Saame.
β	68°	"
γ	107°	Atterberg.
δ	114°	Clève
ϵ	135°	"

The two latter were prepared from the two disulphonic acids recently discovered by Ebert and Merz, by the action of phosphoric chloride. The δ -chloride is soluble in alcohol, and forms large laminæ. The ϵ -chloride crystallises in prisms, and is sparingly soluble.

W. R.

Nitro- and Amido-naphthylsulphonic Acids and their Derivatives. (Part II.) By P. T. CLÈVE, *Bull. Soc. Chim.* [2], xxvi, 241—244).—*Naphthionic acid*, $C_{10}H_6NH_2.SO_3H$, was prepared both by Piria's method (acting on nitronaphthalene with ammonium bisulphite), and by Schaal and Schmidt's (acting on naphthylamine with sulphuric acid), and it was proved that both these processes give the same acid. By the action of nitrous acid it is converted into *diazo-*

naphthionic acid, $C_{10}H_5 \left\{ \begin{matrix} N \\ SO_2 \end{matrix} \right\} > H$, a yellowish crystalline powder,

which detonates by percussion or by heat, and evolves nitrogen when heated with water. Excess of nitrous acid converts it into dinitronaphthol, $C_{10}H_5(NO_2)_2OH$, owing to the action of the nitric acid formed on the oxynaphthylsulphonic acid resulting from the decomposition of the diazo-acid. The melting point of the dinitro-naphthol was found to be 130° .

A dioxynaphthalene cannot be prepared from diazo-naphthionic acid by the action of caustic potash.

A *dichloronaphthalene* crystallising in prisms and in colourless needles, and melting at 67.5° , was obtained by converting the diazo-acid into chloronaphthylsulphonic acid by heating it with hydrochloric acid, and distilling the potash salt with phosphoric chloride. The product has the formula, $C_{10}H_5Cl.SO_2Cl$, and when redistilled with phosphoric chloride gives the dichloronaphthalene. It corresponds with that obtained by Faust and Saame, and called by them *β-dichloronaphthalene*, also with that obtained by Atterberg of Upsala by acting on *α*-nitronaphthol with phosphoric chloride. This shows that naphthionic acid belongs to the same series as *α*-nitronaphthalene, which contains the groups NO_2 and OH in the same benzene ring, and next each other.

The following bodies have, doubtless, an analogous structure:—

	Melting point.	
<i>β</i> -Dichloronaphthalene.....	68°	$C_{10}H_5Cl_2$.
Nitrochloronaphthalene	85	$C_{10}H_5(NO_2)Cl$.
Hydonaphthoquinone.....	176	$C_{10}H_5(OH)_2$.
Naphthoquinene	125	$C_{10}H_5O_2$.
Naphthoic acid, giving		$C_{10}H_5(CO.OH)_2$.
Naphthoic anhydride	266	$C_{10}H_5(CO)_2O$.
<i>α</i> -Naphtholsulphonic acid	101	$C_{10}H_5SO_3H.OH$.
<i>α</i> -Carbonaphthalic acid	185—186	$C_{10}H_5(OH)CO.OH$.
Naphthionic acid		$C_{10}H_5(NH_2)SO_3H$.
<i>α</i> -Nitronaphthol	164	$C_{10}H_5(NO_2)OH$.
<i>α</i> -Nitrosonaphthol of Fuchs	175—185	$C_{10}H_5(NO)OH$.
<i>α</i> -Amidonaphthol.....		$C_{10}H_5(NH_2)OH$.
<i>α</i> -Nitronaphthylamine	191	$C_{10}H_5(NO_2)NH_2$.
Diamidonaphthalene, of Liebermann and Dittler.....		$C_{10}H_5(NH_2)_2$.
Nitracetonaphthalide and its derivatives		$C_{10}H_5(NO_2)NHC_2H_5O$.
		W. R.

Note on some New Derivatives of Anthracene. By W. H. PERKIN (*Chem. News*, xxxiv, 145).—Anthracene dibromide, crystallising in flat oblique prisms, which turn yellow and opaque at the ordinary temperature with evolution of hydrobromic acid, is prepared by treating anthracene with a solution of bromine in carbon disulphide. It dissolves with difficulty in carbon disulphide, alcohol and ether. When the dibromide is heated, the monobromide is formed; it may also be prepared by acting with the theoretical amount of bromine dissolved in carbon disulphide on anthracene. It melts at 100° ; dissolves in benzene and carbon disulphide, also in alcohol and glacial acetic acid; crystallises in long needles, and combines with picric acid.

The dichloride separates out as a white precipitate on passing chlorine into a one per cent. solution of anthracene cooled to 0° . It is very unstable. It dissolves sparingly in alcohol, ether, benzene, acetic acid, and carbon disulphide. On fusing it, monochloranthracene is formed. This compound crystallises from alcohol in golden-yellow, flat needles, and melts at 103° ; dissolves easily in ether, benzene, carbon disulphide, and alcohol, and moderately in acetic acid. Its compound with picric acid crystallises in beautiful scarlet needles.

W. R.

Simultaneous Formation of two. Trioxyanthraquinones, and Synthesis of a New Isomeride of Purpurin. By A. ROSENSTIEHL (*Compt. rend.*, lxxxiii, 827—830).—Schützenberger, in making approximate analyses of commercial purpurin, mentions as one of its constituents, a yellow substance, dyeing yellow with alumina as a mordant. The author, during his researches on the colouring matters of madder, amassed several grams of this substance. As it is an isomeride of purpurin, $C_{14}H_2O_6$, he gives it the name of *ε-purpurin*. It is obtained by boiling pseudopurpurin with boiling water, whereupon water is absorbed, and oxygen evolved; and hydrated purpurin and the new body are formed. It was separated from the purpurin by oxidising the latter with potassium permanganate, or by exposing its alkaline solution to air. Any remaining purpurin is removed as a lake with iron. The yield of the new substance is very small. It is a light orange-coloured powder which begins to melt at 180° , and sublimes with partial decomposition. It is more easily soluble in water than the other madder dyes, and dissolves easily in alcohol, acetic acid, benzene, and chloroform. It is soluble in strong sulphuric acid, and is reprecipitated by water. With alkalis it gives red compounds, intermediate in colour between purpurin and purpuroxanthin. The lime and baryta lakes are sparingly soluble in boiling water; it dissolves in a hot solution of alum, and is deposited on cooling. With alumina mordants, it gives an orange colour, three or four of Chevreul's tables; it is saturated only in presence of an equivalent of calcium acetate. This dye does not resist the operations of soaping and clearing; it gives no colour with iron mordants.

It has the following relations to the oxyanthraquinones: tetraoxyanthraquinone, or pseudopurpurin, $C_{14}H_4(OH)_4O_2$, when heated with water to 100° loses an atom of oxygen, and gives rise to two trioxy-

quinones, $C_{14}H_6(OH)_2O_2$, one giving a red, and the other an orange colour with alumina. These two, when reduced in alkaline solution, give a single dioxanthraquinone, $C_{14}H_6(OH)_2O_2$, Schützenberger's purpuroxanthin. The latter, when oxidised in hot solution, gives a purpurin which dyes red; in cold solution a purpurin dyeing orange. All these substances exist in madder as glycosides.

ϵ -Purpurin, when treated with phosphorus in alkaline solution, loses an atom of oxygen, and is converted into a dioxanthraquinone, purpuroxanthin; when boiled with an alkali, it undergoes molecular transformation into purpurin. ϵ -Purpurin can be synthetically prepared; by oxidising alizarin purpurin is formed; from purpurin, its isomeride can be prepared; by reduction purpuroxanthin is formed; and the latter when oxidised yields ϵ -purpurin. W. R.

Action of Quicklime on Phenanthrenequinone. By R. ANSCHÜTZ and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, ix, 1400—1403).—When phenanthrenequinone is distilled with common soda-lime, it yields as chief product diphenyl, as Gräbe has already shown. On using a soda-lime sold as prepared from sodium, no diphenyl was formed, but (1) fluorene; (2) a red body of high boiling point, which also accompanies the diphenyl; (3) a white compound melting at 150° . When only quicklime is used, the products consist of diphenyl ketone melting at 83 — 84° and fluorene. C. S.

Nitrophenanthrenequinone. By R. ANSCHÜTZ and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, ix, 1404).—This compound is obtained by boiling the quinone with a mixture of common and fuming nitric acid; it forms golden yellow plates, melting at 257° , and is almost insoluble in alcohol and sparingly soluble in glacial acetic acid. On distilling it with soda-lime, a volatile base is formed. C. S.

Herapathite and similar Acid Periodides. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], xiv, 213—268).—The first section of this paper consists of an historical introduction; the second treats of the methods of analysis employed by the author; and the third gives an account of the bodies prepared and examined.

A. QUININE COMPOUNDS.—Quinine forms many compounds similar to herapathite, and they may be divided into two series. One, to which herapathite proper belongs, contains three molecules of sulphuric acid to four of quinine; the other one molecule of acid to two of quinine.

The first series consists of tolerably stable compounds, while the salts of the other-series are prone to decomposition, with formation of compounds belonging to the first series.

1st *Herapathite*, $4C_{20}H_{24}N_2O_2 \cdot 3SH_2O_4 \cdot 2HI \cdot I_4 + xH_2O$, is best prepared by dissolving neutral quinine sulphate in the calculated quantity of sulphuric acid, warming with alcohol up to boiling, mixing with the calculated quantity of hydriodic acid and iodine, the first in aqueous, the second in alcoholic solution, and allowing the whole to cool slowly.

Herapathite is found to contain unaltered quinine, and one-third of the iodine is present as hydriodic acid.

2nd *Sulphato-periodide of Quinine*, $8C_{20}H_{24}N_2O_2 \cdot 6H_2SO_4 \cdot 4HI \cdot I_{10}$.—There are several methods of obtaining this compound. One is to dissolve one molecule of neutral quinine sulphate with two molecules of sulphuric acid in alcohol, and to add to the solution heated to boiling one atom of iodine dissolved in alcohol. The crystals of this salt have a metallic lustre, and are of an olive-grey colour, between the grass-green of herapathite and the bronze-yellow of the next compound. They are more soluble in warm than in cold alcohol, but not so soluble as herapathite.

3rd *Sulphato-periodide of Quinine*, $4C_{20}H_{24}N_2O_2 \cdot 3H_2SO_4 \cdot 2HI \cdot I_6 + 2H_2O$.—This compound may be formed by addition of 1 part of iodine to $3\frac{1}{2}$ parts of herapathite in alcoholic solution. It crystallises in long flat needles or in plates of the same form as herapathite. It is of a bronze-yellow colour, and is less soluble than herapathite in hot alcohol. On recrystallisation it is decomposed into iodine and the previous compound.

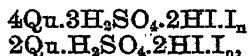
4th *Sulphato-periodide of Quinine*, $8C_{20}H_{24}N_2O_2 \cdot 6H_2SO_4 \cdot 4HI \cdot I_{14} + 4H_2O$.—Formed in the attempt to produce the 7th compound (see below) from the calculated quantities of quinine sulphate, hydriodic acid and iodine. Bronze-yellow brownish needles with fine metallic lustre. It is isomorphous with the previous compound.

5th *Sulphato-periodide of Quinine*, $2C_{20}H_{24}N_2O_2 \cdot H_2SO_4 \cdot 2HI \cdot I_2$.—Obtained by mixing an almost cold solution of one molecule of neutral quinine sulphate in alcohol with two atoms of iodine dissolved in hot alcohol, and allowing the mixture to stand for two hours. It consists of long, red, brilliant needles, which in air become changed into a black glassy mass.

6th *Sulphato-periodide of Quinine*, $2C_{20}H_{24}N_2O_2 \cdot H_2SO_4 \cdot 2HI \cdot I_4$.—The calculated quantity of neutral quinine sulphate, hydriodic acid and iodine is dissolved in hot alcohol, and the solution is mixed with so much hydriodic acid that nothing crystallises out on cooling. On cautious addition of water, olive-green laminæ separate. This compound is more soluble in hot than in cold alcohol, but cannot be crystallised from this solvent. Herapathite is deposited on cooling.

7th *Sulphato-periodide of Quinine*, $2C_{20}H_{24}N_2O_2 \cdot H_2SO_4 \cdot 2HI \cdot I_8$.—May be obtained in several ways—for instance by mixing a hot alcoholic solution of herapathite with a large quantity of solution of iodine, diluting somewhat with water, and allowing the mixture to stand. This compound forms brilliant black needles and laminæ with a greenish reflection. If washed with too strong a solution of alcohol, the crystals resemble potassium permanganate in appearance. They cannot be recrystallised, for although slowly soluble in alcohol, another compound, not yet accurately examined, separates on cooling.

In addition to the two classes of salts above described—



a third seems to exist, of the composition $3Qu \cdot 2H_2SO_4 \cdot 2HI \cdot I_n$. The salts of this series have not yet been examined with sufficient accuracy

to settle their formulæ with certainty, but the author's results are as follows:—

No. 1. $3C_{20}H_{24}N_2O_2 \cdot 2H_2SO_4 \cdot 2HI \cdot I_3$ (?).—This compound consists of groups of fine needles which are blue by transmitted light when in thin layers. It is obtained during the recrystallisation of the next substance.

No. 2. $3C_{20}H_{24}N_2O_2 \cdot 2H_2SO_4 \cdot 2HI \cdot I_5 \cdot H_2O$ (?).—Consists of olive-grey laminæ, which separate from a hot alcoholic solution of acid sulphate of quinine on addition of varying quantities of solution of iodine.

No. 3. $3C_{20}H_{24}N_2O_2 \cdot 2H_2SO_4 \cdot 2HI \cdot I_8$ (?).—Obtained only once in a pure state from one molecule of neutral sulphate of quinine, two molecules of normal sulphuric acid, and 200 c.c. of an old solution of iodine, containing 16·8 grams of free iodine. All attempts to reproduce this body with a freshly-prepared solution of iodine failed. It consists of olive-green needles with metallic lustre, which polarise light in exactly the opposite direction to herapathite.

B. COMPOUNDS OF METHYL-QUININE.—1st *Sulphato-periodide of Methyl-quinine*, $2C_{20}H_{24}N_2O_2(CH_3)I \cdot H_2SO_4 \cdot I_4$.—This compound is obtained by slowly cooling a mixture of the theoretical quantities of methyl-quinine iodide and sulphuric acid with about four-fifths of the calculated quantity of iodine in alcoholic solution at a temperature of about 60°. It consists of reddish-brown needles, often several centimeters in length, which are easily soluble in hot alcohol.

2nd *Sulphato-periodide of Methyl-quinine*, $2C_{20}H_{24}N_2O_2(CH_3)I \cdot H_2SO_4 \cdot I_6$.—Most easily prepared by slowly cooling a mixture of methyl-quinine iodide, sulphuric acid, and iodine (in the calculated quantities, from a hot alcoholic solution. It consists of very fine brilliant brown laminæ, soluble with difficulty even in hot alcohol.

3rd *Sulphato-periodide of Methyl-quinine*, $4C_{20}H_{24}N_2O_2(CH_3)I \cdot 2H_2SO_4 \cdot I_{14}$.—Prepared by warming an alcoholic solution of No. 1 to 60°, and adding an alcoholic solution of four atoms of iodine of the same temperature. It consists of brilliant, almost black laminæ, which must be filtered off from the still warm solution and washed with alcohol at about 60°. The temperature must be kept down, or else the product consists chiefly of No. 2. It is soluble with difficulty in hot alcohol.

4th *Sulphate-periodide of Methyl-quinine*, $4C_{20}H_{24}N_2O_2(CH_3)I \cdot 2H_2SO_4 \cdot I_{18}$.—Obtained by mixing a hot alcoholic solution of No. 1 with a large excess of a cold solution of iodine. It consists of long, thin, almost black needles, with a greenish metallic lustre. The crystals dissolve with difficulty in hot alcohol.

Compounds containing four molecules of methyl-quinine to three of sulphuric acid could not be obtained.

C. COMPOUND OF QUININE-METHYL-QUININE.—An attempt was made to prepare herapathite with methyl-quinine in place of hydriodic acid, by mixing the calculated quantities of methyl-quinine iodide, quinine sulphate, and iodine, in hot alcoholic solution. The result was a compound of herapathite with No. 1 sulphato-periodide of methyl-quinine, and water. This body crystallises in dark chocolate-brown masses, which appear under the microscope as carmine-red, intertwined hairs. The water is given off at 100°. The compound dissolves with some difficulty in hot alcohol.

G. T. A.

Oxidation of Cholic Acid with Potassium Dichromate and Sulphuric Acid. By H. TAPPEINER (*Zeitschr. für Biologie*, xii, 60—74).—Cholic acid was prepared from bile by boiling with baryta-water, was recrystallised till perfectly white and pure, and was then oxidised in portions of a gram by a mixture of 10 grams potassium dichromate, 15 sulphuric acid, and as much water as occupied three times the volume of the acid, the whole being gently heated in a sand-bath, an inverted condenser being attached to the flask. After 6—10 hours white masses floated on the surface of the liquid, and also an oily film which solidified on cooling. On filtering and distilling the filtrate, acetic acid passed over, and traces of a solid acid were left in the retort. The solid substance left on the filter dissolved readily in alkalis and was reprecipitated by acids. The precipitate was washed and suspended in water. On distilling the whole, oily drops passed over, solidifying to white crusts on cooling. This took place so slowly, however, that distillation for a month was necessary to effect the complete expulsion of the volatile acid. The white crusts thus obtained melted at 53—54°, and gave a barium salt containing 20.43 per cent. Ba, agreeing with a mixture of stearate and palmitate.

The non-volatile residue dissolved perfectly in alcohol, and crystallised therefrom in needles which did not melt at 250°, but melted with decomposition at a higher temperature. It formed a barium salt soluble in water, and by this means a more convenient mode of separating the volatile acid was obtained, as the barium salt of the volatile acid is insoluble in water. When kept for a long time at 150° it slightly browned. On analysis of the acid and its barium salt, numbers were obtained leading to the formula $C_{40}H_{80}O_{12}$, the barium salt being $Ba_5(C_{40}H_{80}O_{12})_2$, i.e., the acid being pentabasic. The silver salt is a white non-crystalline curdy precipitate of analogous composition, $C_{40}H_{80}Ag_5O_{12}$.

Larger quantities of cholic acid were treated, and the volatile and non-volatile acids separated as barium salts. On repeatedly crystallising the volatile acid from alcohol, the melting point rose, and finally a body was obtained melting at 67°, and giving numbers agreeing with the formula $C_{22}H_{42}O_3$. Another acid was also isolated (by fractional precipitation as barium salt), agreeing with the formula $C_{15}H_{30}O_2$, and melting at 54°. Hence it appears that there is some reason for assigning a connection between bile and fatty acids.

The aqueous chromic liquid from which these acids had separated in the solid form, yielded on evaporation a small quantity of crystalline scales. These consisted of an acid melting at 196—198°, and giving numbers agreeing with the formula $C_{41}H_{85}O_{22}$, the silver salt being $C_{41}H_{85}Ag_{10}O_{22}$, and the barium salt $C_{41}H_{85}Ba_5O_{22}$. [The analytical numbers agree better with $(C_{41}H_{85}O_{22})_2Ba_5$]. C. R. A. W.

The Fluorescent Body in Atropa Belladonna. By R. FASSBENDER (*Deut. Chem. Ges. Ber.*, ix, 1357—1358).—This body, which is contained in all parts of the plant, is distinguished by its strong fluorescence and stability, as shown by the following experiment. Two unripe berries were crushed with a little water, the mass dried on a water-bath, the residue exhausted with alcohol, the solution again

evaporated, and the remainder dissolved in water. The filtered solution was shaken at a gentle heat with animal charcoal, which takes up the compound. On then digesting it with alcohol and a little ammonia, a liquid is obtained showing a beautiful blue fluorescence, even if very dilute. The solution may be evaporated repeatedly without the compound losing its fluorescence, which reappears on the addition of ammonia.

C. S.

Styrax. By J. H. VAN'T HOFF (*Deut. Chem. Ges. Ber.*, ix, 1339—1341).—In reply to Berthelot, the author maintains the correctness of his former observations on styrolene and cinnamene (this Journal, 1876, ii, 703).

C. S.

Note on Litmus. By H. W. MITCHELL (*Chem. News*, xxiv, 140—141).—Wartha has separated four organic bodies from litmus. The first is obtained by treating commercial litmus with alcohol of about 90 per cent., filtering cold, and boiling the clear tincture; whereupon indigo is precipitated as a fine powder, according to the author. The second body is obtained by evaporating the violet-red mother liquor; it is a beautiful red, or, from many varieties, green fluorescent substance, indifferent to acids. The litmus residue left after treatment with alcohol is digested with distilled water for 24 hours, after which the deep-coloured solution is evaporated on the water-bath, and the residuary extract is treated several times with absolute alcohol containing a little glacial acetic acid, and again evaporated, until it forms a brown powdery mass. This mass is now exhausted with absolute alcohol and acetic acid, whereby a large quantity of a scarlet-red body is dissolved, which resembles orcein, and becomes purple-red in place of blue with ammonia. The portion of the brown powder insoluble in the acidified alcoholic solution consists of litmus colouring matter in a very pure form, so pure in fact that by means of it the carbonated alkaline earths contained in spring-waters may be titrated with as great delicacy as by the use of cochineal tincture, which is far from being the case with crude litmus.

To get this substance perfectly pure, it is first washed with absolute alcohol, then dissolved in a small quantity of water and thrown into a large excess of alcohol, and the flocculent purple precipitate is collected and again thoroughly washed with alcohol. In repeating the above experiments, the author confirms Wartha's results in every particular, save as regards the indigo, which could not be obtained by boiling the alcoholic tincture. The fluorescent body above mentioned is violet or purple, and gives a solution in alcohol of a similar colour, which shows a beautiful green fluorescence with sunlight, and with the spectroscope gives a very characteristic absorption-band in the green, together with an almost total absorption of the violet end of the spectrum. It is soluble in water, amyl alcohol, and common ether, very soluble in alcohol, but is insoluble in carbon bisulphide, chloroform, petroleum, naphtha, and turpentine. The solutions, both in amyl alcohol and in ether, exhibit a beautiful fluorescence, but the ethereal solution shows the absorption-band in the green only very faintly. The body which resembles orcein shows a very faint fluorescence; its alcoholic solution

gives a spectrum in which the absorption is characteristic and quite distinct from that of the last; it is slightly soluble in water, very soluble in alcohol, but seems to be insoluble in ether, chloroform, carbon disulphide, and petroleum naphtha. The pure litmus colouring matter is insoluble in alcohol, ether, chloroform, bisulphide of carbon, and petroleum naphtha, very soluble in water. It turns blue with ammonia, and yields in alkaline solutions a beautiful violet-lake with alumina, one of a pale violet colour with stannous acetate, and deep blue lakes with calcium and barium.

The residue left after extracting the pure litmus dissolves to some extent in hydrochloric acid. The residue insoluble in hydrochloric acid consists mostly of fine sand, but yields some colouring matter to strong ammoniac hydrate. About 25 grams of the pure colouring matter, 15 grams of the body like orcein, and 10 grams of the fluorescent body, were obtained per ounce of litmus.

D. B.

Physiological Chemistry.

Quantitative Analyses of Blood. By G. BUNGE (*Zeitschrift f. Biologie*, xii, 191—216).—The following are analyses of the blood of pigs, horses, and oxen:—

I.—Defibrinated Pig's Blood.

Per 1,000 parts of blood-corpuscles.	Per 1,000 parts of serum.
Water 632.1	Water 919.6
Solid constituents 367.9	Solid constituents 80.4
Hæmoglobin 261.0	Albumin 67.7
Albumin 86.1	Other organic substances 5.0
Other organic substances 12.0	Inorganic substances 7.7
Inorganic substances 8.9	Potash 0.273
Potash 5.543	Soda 4.272
Magnesia 0.158	Lime 0.136
Chlorine 1.504	Magnesia 0.038
Phosphoric acid 2.067	Oxide of iron 0.011
	Chlorine 3.611
	Phosphoric acid 0.188

II.—Defibrinated Horse's Blood.

Per 1,000 parts of blood-corpuscles.	Per 1,000 parts of serum.
Water 608.9	Water 896.6
Solid constituents 391.1	Solid constituents 103.4
Potash 4.92	Potash 0.27
Chlorine 1.93	Soda 4.43
	Chlorine 3.75

III.—*Defibrinated Ox-blood.*

Per 1,000 parts of blood-corpuscles.	Per 1,000 parts of serum.
Water	Water
Solid constituents	Solid constituents
Hæmoglobin	Albumin
Albumin	Other organic substances
Other organic substances	Inorganic substances
Inorganic substances	Potash
Potash	Soda
Soda	Lime
Magnesia	Magnesia
Chlorine	Oxide of iron
Phosphoric acid	Chlorine
	Phosphoric acid

H. H. B. S.

Can Inorganic Constituents be withdrawn from the Bones by the introduction of Lactic Acid into the Intestines? By E. HUISS (*Zeitschrift f. Biologie*, xii, 151—169).—The decrease in the amount of the inorganic constituents of the bones which is known to take place during the progress of certain diseases has been referred by some to defective nourishment, but by others to the solvent action of an accumulation of acid in the body. This latter view is supported by Marchand (*Jour. f. prakt. Chem.*, xxvii, 93), who states that the urine of a child suffering from rachitis was found to contain more than the normal amount of phosphate of lime, in addition to considerable quantities of lactic acid, and that its bones subsequently proved to be deficient in lime-salts, but to contain an excess of organic matter. He consequently attributes this disease to a solution of bone-earth by lactic acid, derived from the fermentation of carbohydrates in the intestines, and induced by a diseased state of the mucous membrane of the stomach; so that, according to his views, rachitis proceeds in the first instance from a disordered state of the digestive organs. Beneke, however, believes this solution and secretion of phosphate of lime to be brought about principally by oxalic acid, though this seems very improbable; and it has moreover been asserted by Buchheim and Piotrowky, that oxalic acid is without influence upon the excretion of lime.

Researches on the origin of bone-diseases have also been made by Heitzmann, who asserts that rachitis and osteomalacia were produced in certain animals to which he had administered lactic acid, by subcutaneous injection or by mixture with the food. Since, however, he gave no analysis of the diseased bones to prove a diminution in mineral constituents, and as his results also for other reasons did not seem to be conclusive, the author was induced to re-investigate the subject.

For this purpose a small spaniel dog, 18 months old, and weighing 4,701 grams, was fed daily with food containing lactic acid, in quantities at first of 1—2 grams, but afterwards increased to 4—6 grams, and finally to 7—9 grams. In order that its dung and urine might be collected without loss, it was kept during the whole time the experiment lasted in a confined space, from which it was only removed from time

to time to be weighed. At the expiration of 308 days, it was bled to death through an opening made in the carotid artery.

Throughout the whole time the animal had never shown any symptoms of disease, and Professor Bollinger, who made a careful post-mortem examination, failed to discover the least signs of rachitis or osteomalacia. In order, however, to ascertain whether the lactic acid had withdrawn any mineral constituents from the body, the different parts were separately weighed and submitted to analysis; but in every case the results obtained were perfectly normal, showing no deficiency whatever in the alkaline earths.

Lastly, the total amount of lime and magnesia contained in the food consumed was found to be precisely the same as that excreted in the dung and urine, thus proving conclusively that none could have been withdrawn by the lactic acid.

The question then remains as to what became of the lactic acid. The author believes it must have been decomposed on passing through the dog's body, since no appreciable quantity could be detected in the urine.

H. H. B. S.

Researches on the Formation of Hippuric Acid in the Organisms of Herbivorous Animals supplied with different kinds of Fodder. By H. WEISKE (*Zeitschrift f. Biologie*, xii, 241—265).—Two fully-grown wethers, of equal age and similar breed, received each 2 lbs. of meadow hay daily. Their urine was at the same time carefully collected and examined, and the figures thus obtained give the following mean results for each animal per day:—

	Consumption of water.	Quantity of urine.	Sp. gr.	Nitrogen.	Hippuric acid.
No. I.....	1143 grs.	520 c.c.	1·060	9·11 grams.	15·45 grams.
No. II.....	—	820 c.c.	1·043	9·80 grams.	16·07 grams.

The mean daily production of hippuric acid was, therefore, 15·76 grams—a quantity which closely approximates to that found by Hofmeister.

Animal No. 1 then received in addition 15 grams of common salt, with the following result:—

	Description of food.	Consumption of water.	Quantity of urine.	Spec. grav.	Nitrogen.	Hippuric acid.
Mean of four days' results ..	2 lbs. of meadow-hay + 15 grams NaCl.	1684 grams	864 c.c.	1·054	9·42 grams	16·09 grams

The addition of salt to the food was, therefore, followed by an increase in the consumption of water and in the volume of urine, as well as to a slight extent in the quantity of nitrogen and hippuric acid. This result is just the reverse of that obtained by Grouven, who states that with cattle the addition of salt to the food caused a very

considerable decrease in the quantity of hippuric acid secreted with the urine. (*Physiolog. Chem. Fütterungsversuche. Berlin, 1864*).

Experiments were next made with mixtures of hay with wheat, beans, and potatoes respectively, in the proportion of one part of dried hay to one part of the dried substance of the other ingredient. The experiments extended in each case over four days, and gave the following mean results:—

Description of food.	Consumption of water.	Quantity of urine.	Sp. gr.	Hippuric acid.
1 lb. meadow-hay .. } + 1 lb. wheat	1293 grams	517 c.c.	1·039	6·32 grams
1 lb. meadow-hay .. } + 1 lb. beans	1660 "	621 "	1·054	4·67 "
1 lb. meadow-hay .. } + 4 lbs. potatoes....	963 "	538 "	1·051	2·84 "

This admixture of easily digestible foods with the hay must, therefore, have diminished the secretion of hippuric acid, since it has been previously shown that 1 lb. of hay will produce about 8 grams.

The effect of dosing with salicylic acid and benzoic acid was then tried, the precaution being taken of feeding with hay alone for one day on changing from one acid to the other. The results were as follows:—

Date.	Description of food.	Consumption of water.	Urine.					
			Quantity.	Sp. gr.	Nitrogen.	Hippuric acid.	Salicylic acid.	Salicylic acid.
March 11 to 14	2 lbs. hay.	grams. —	c.c. 820	1·043	9·80	16·07	—	—
15 to 17	2 lbs. hay + 5 grams salicylic acid.	1188	761	1·053	9·34	15·41	3·00	2·11
18 to 19	2 lbs. hay + 10 grams salicylic acid.	868	642	1·059	10·76	14·23	6·59	4·10
20	2 lbs. hay + 15 grams salicylic acid.	1520	1257	1·083	11·43	18·78	9·01	4·84
21	2 lbs. hay.	1875	690	1·047	10·77	16·05	2·04	0·98
22 to 24	2 lbs. hay + 5 grams benzoic acid.	1423	663	1·047	10·44	25·11	—	—
25 to 27	2 lbs. hay + 10 grams benzoic acid.	1490	831	1·048	10·89	31·74	—	—
28 to 30	2 lbs. hay + 15 grams benzoic acid.	1503	873	1·051	11·09	36·49	—	—
March 31 to April 3	2 lbs. hay.	1620	865	1·044	9·92	16·00	—	—

These figures show that when a small dose of salicylic acid is administered, a portion only is secreted as salicyluric acid, but that this portion is always greater than that which passes into the urine unchanged. This was also noticed by Bertagini, who swallowed 0.25 grams of salicylic acid per hour for two days, and found in his urine unchanged salicylic acid as well as salicyluric acid.

It is interesting to notice the extreme regularity with which the hippuric acid was secreted; thus the average per day was :—

From 11th to 14th March. .	On feeding with hay alone	16.07 grams.
„ 15th „ 20th „ ..	„ hay + salicylic acid	16.14 „
On the 21st March	On feeding with hay alone	16.05 „
From 31st March to 3rd April	„ „	16.00 „

Kletzinsky's supposition, that the hippuric acid is formed at the expense of urea is confuted by these experiments, for it will be seen that the increase of hippuric or salicyluric acid was nearly always accompanied by a corresponding increase of nitrogen, the only exception being on the administering of 5 grams of sulphuric acid from 15th to 17th March.

Separate experiments were made with peas, linseed, wheat, and oats respectively, but no hippuric acid could be separated from the urine in any of these cases, although the liquid was allowed to stand for 48 hours. The same negative result was obtained on feeding with unpeeled potatoes, as well as with pea and bean straw, but the straw of cereals behaves differently in this respect. Animal No. 1 was fed for seven days upon wheat-straw, and afterwards for the same length of time upon oat-straw, with the following results :—

Average per day.	Description of food.	Con- sumption of water.	Urine.			
			Quantity.	Sp. gr.	Nitrogen.	Hippuric acid.
June.		grams.	c.c.			
From 14 to 16	1 lb. wheat straw.	1337	427	1.035	—	2.51
„ 21 to 23	1½ lb. oat straw.	1160	313	1.035	1.95	3.24

So that almost precisely the same quantity of hippuric acid was produced by the consumption of 1 lb. of either wheat or oat straw.

These results disclose a remarkable relation between the amount of nitrogen and hippuric acid found in the urine after the assimilation of hay and straw. Thus, sheep No. 1, when fed exclusively upon hay, secreted in 24 hours 9.11 grams nitrogen to 15.45 grams hippuric acid; consequently, at the same ratio the amount of hippuric acid secreted for 1.95 gram nitrogen should be 3.31 grams, and 3.24 grams was actually found.

The urine remained always distinctly alkaline, whereas Henneberg

and Stohmann found that the urine of cattle gave under similar conditions an acid reaction.

If hay is soaked for 24 hours in a cold dilute (1.25 per cent.) solution of sulphuric acid or potash, and afterwards well washed and dried, its property of forming hippuric acid on passing through the body becomes quite changed. This will be seen from the following experiments:—

Date.	Description of food.	Consumption of water.	Urine.		
			Quantity.	Sp. gr.	Hippuric acid.
Sept. 10	Hay treated with sulphuric acid.	1200 grams.	1232 c.c.	1.009	—
" 11		1580 "	1250 "	1.006	—
" 12		690 "	738 "	1.017	—
" 13		690 "	740 "	1.016	—
Sept. 26	Hay treated with potash.	1030 grams.	552 "	1.021	2.62 grams.
" 27		1030 "	518 "	1.023	3.02 "
" 28		810 "	440 "	1.027	4.66 "
" 29		1090 "	398 "	1.034	3.05 "
Mean	990 grams.	476 c.c.	1.026	3.60 grams.

This complete disappearance of hippuric acid from the urine after the assimilation of hay that has been treated with sulphuric acid completely refutes Meissner and Shepard's theory, ascribing its origin to the cuticular substance, since this is neither destroyed by a solution of sulphuric acid nor of potash of the above strength. Hofmeister, who made similar experiments, found that treatment of hay with boiling water did not interfere with its property of forming hippuric acid, but that this was completely destroyed by treatment with boiling water, alcohol, and boiling solution of potash of 3 per cent. It may, therefore, be assumed that the substance which causes its formation is insoluble in boiling water, partially soluble in solution of potash (1.25 per cent.), and completely soluble in dilute sulphuric acid (1.25 per cent.), as well as in boiling alcohol and solution of potash of 3 per cent.

H. H. B. S.

Alleged Power of Glycerin to replace Sugar. By C. USTIMOWITSCH (*Pflüger's Archiv. f. Physiologie*, xiii, 453—460).—Glycerin, pure or diluted with water, was introduced into dogs or rabbits, either through the jugular vein or by means of a fistula into the stomach, the animal being meanwhile narcotised with morphia.

To augment the excretion of urine, warm beer was in some experiments introduced into the stomach. This exerts no influence upon the action of the glycerin.

The urine was collected both before and after the introduction of glycerin. The original urine from the dog generally showed a reducing action on the cupric salt, but that from the rabbit never.

Within 4 to 15 minutes after the introduction of the glycerin, a

remarkable acceleration in the excretion of urine takes place, the urine being as clear as water. When the rate of excretion reaches its maximum, there is a gradual coloration of the urine, first to straw-yellow, then slowly to red, and finally to blood-red, the coloration being independent of the quantity of glycerin injected. The secretion of urine attains in some cases a maximum of 3 c.c. per minute.

The results of experiments made upon the urine, after elimination of albumin and filtration through animal charcoal, lead to the following conclusions :—

1. Glycerin acts as a diuretic.
2. This action may be considered as due, either to the hygroscopic property of glycerin, or as dependent upon the dilution of the blood.
3. The presence of hæmoglobin in the urine strengthens the second supposition, whilst separate investigations show a loss of corpuscles from the blood.
4. That the reducing power of the urine is referable to the presence of a product of decomposition of the glycerin.
5. That the reducing body is not sugar.
6. The action of glycerin is the same both upon healthy and upon diabetic animals.

F. J. L.

On the Influence which the tying of the Ductus Choledochus exerts upon the amount of Glycogen in the Liver. By E. KULZ and E. FRERICHES (*Pflüger's Archiv. f. Physiologie*, xiii, 460—468).—Wickham Legg found that if the ductus choledochus of a cat were tied, no sugar was found in the urine within five or six days after puncture, whilst, without tying, glycosuria commenced within an hour after puncture. Subsequently v. Wittich found that this tying of the ductus choledochus diminished the quantity of glycogen in the liver, and caused sugar to appear in the urine. This diminution he considered due either to the rapid conversion of glycogen into sugar and extraction by the blood, which would account for the sugar in the urine, or from the liver not producing any more glycogen beyond what existed at the time of tying.

To prove which of these suppositions holds good, experiments have been made upon guinea-pigs and rabbits, which show that the ligature of this duct considerably lessens the amount of glycogen in the liver, whilst at the same time no sugar can be detected in the urine.

Experiments were next performed upon rabbits which had been starved for six days, and then fed with cane-sugar solution through the mouth. The results obtained confirmed the previous ones.

These experiments, as also the observation of Tegg, prove v. Wittich's second supposition to be correct.

F. J. L.

Occurrence of Nuclein in Human Brain. By R. v. JAKSCH (*Pflüger's Archiv. f. Physiologie*, xiii, 469—474).—A substance has been obtained from human brain, which is analogous, physically and chemically, to the nuclein of Miescher. The white substance of the brain contains but a small quantity of nuclein compared with that in the grey, whilst the total amount obtained from the brain of a boy, aged

16, was 3 grams. The nuclein, which is probably not absolutely free from impurity, gave on analysis:—

	No. 1.	No. 2.	
Phosphorus.....	2·08	1·71	
Nitrogen.....	13·12	13·15	
Carbon.....	50·60	50·50	
Hydrogen.....	7·40	7·80	F. J. L.

Chemistry of the Crystalline Lens. By M. LAPTSCHINSKY (*Pflüger's Archiv. f. Physiologie*, xiii, 631—633).—The existing analyses of the crystalline lens not being sufficiently complete, further analyses have been made, the eyes of oxen having been taken for the purpose, and those methods of analysis employed which are given in *Höppe-Seyler's Handbook of Physiological Chemical Analysis*.

Of four analyses the average result obtained was:—Albumin, 34·93 per cent.; Lecithin, ·23; Cholesterin, ·22; Fat, ·29; Soluble salts, ·53; Insol. salts, ·29. The quantity of globulin found was 24·62 per cent.; therefore the amount of soluble albumin was about 11·0 per cent. A globulin-substance was isolated, which in its actions resembled vitellin, but was marked by its great purity, whereas the vitellin obtained from the yolk of a hen's egg is mixed with considerable quantities of lecithin and nuclein. The quantity of lecithin found was inconsiderable. The cholesterin varied greatly in quantity. Fat is not so considerable as is generally supposed, the lecithin, cholesterin, and fat together being generally less than 1 per cent. The ash of the soluble salts gave an alkaline reaction, effervesced with acids, and contained phosphoric acid, chlorine, sulphuric acid, potash, and soda.

F. J. L.

The Fermentation of Urine; in reference to a communication by Pasteur. By H. CH. BASTIAN (*Compt. rend.*, lxxxiii, 362).—This paper maintains that urine and many other organic acid liquids are capable of the spontaneous production of bacteria. Such liquids, in which the germs of bacteria had been killed by heating, would remain sterile at 25°, but at 50° would spontaneously produce the bacteria. Tyndall entirely disagrees with the author, and coincides with the views of Pasteur.

C. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Absorption of free Nitrogen by the Proximate Principles of Vegetables under the influence of Atmospheric Electricity. By M. BERTHELOT (*Compt. rend.*, lxxxiii, 677—682).—By some previous experiments detailed in the *Compt. rend.*, lxxxii, 1283, it was shown that free nitrogen is directly absorbed by organic substances, under the influence of the electric current. The absorption occurs with pure dry nitrogen and the hydrocarbons, oxygen being absolutely excluded, with lignin, or with moist dextrin, and it also

takes place if air be substituted for pure nitrogen. In those experiments the electricity was developed of enormous tensions by a large Ruhmkorff coil, the conditions being therefore comparable to the tensions produced between the clouds and the ground, during a thunder-storm, and the application of the results to vegetation was legitimate for those exceptional conditions.

The present series of experiments show that the fixation of the nitrogen occurs equally, under the influence of the far weaker electric tensions which are incessantly produced in the air.

The apparatus employed consisted of two glass tubes, one within the other, the interior surface of the inner one being coated with a leaf of silver or platinum, and connected by a platinum wire passing through both tubes with a conductor, electrolysed by the atmosphere. A sheet of tin-foil is rolled round the outer tube, and is connected with the ground. The space separating the edge of the tin-foil from the platinum wire is coated with shellac. Into the annular space between the two tubes is introduced the matter to be operated upon, such as strips of moist filter-paper, or a little strong solution of dextrin, and then that space is filled with nitrogen. The difference of electric tension between the two armatures is the difference of the potential between the ground, and a layer of air two meters above it. In some of the apparatus the inner tube was dispensed with, the inner armature being in contact with the organic substances acted upon.

The experiments lasted about two months, the average electric tension being about that of $3\frac{1}{2}$ elements Daniell, the absolute value having oscillated between + 60 to - 180, Daniell.

In every case, without exception, whether the tubes were open, or hermetically closed, the nitrogen was fixed by the organic substance, forming a nitrogenous compound, which was decomposed by soda-lime, with evolution of ammonia. No indication of the formation of nitric acid by the electric current of this feeble tension, was found.

C. H. P.

The Metamorphoses of the Groups COOH , CH.OH , CH_3 , and CH_2 , in the Living Plant. By A. STUTZER (*Deut. Chem. Ges. Ber.*, ix, 1395—1397).—When young growing plants of *Brassica rapa* are placed in air containing no carbon dioxide, they continue to grow, if they are fed with calcium oxalate or tartrate. But if any carbon dioxide that may be formed by the decomposition of these acids be removed by caustic soda, only those fed with tartaric acid continue to live; they may also be fed with glycerin, or with ferric succinate, which, however, does not act so favourably as the tartrate. From the results it is concluded that the carboxyl-group can be assimilated by plants only after it has been oxidised to carbon dioxide, while alcoholic groups (or methene) are taken up directly. C. S.

Action of Boric Acid and of Borates on Vegetation. By EUG. PÉLIGOT (*Compt. rend.*, lxxxiii, 688).—Even very small quantities of boric acid, either free or in combination, are fatal to plants. It is suggested that they may also be deleterious to animals, and if so the foods preserved by means of borax, such as fresh meats, received from

Buenos Ayres, even though washed before use, might be injurious to the persons eating them. This question is being investigated.

C. H. P.

Organic Constituents of Barley and Malt. By G. KÜHNEMANN (*Deut. Chem. Ges. Ber.*, ix, 1385—1388).—The sinistrin which the author has discovered in barley disappears almost completely during germination, but is always contained in wort and beer, as malt contains broken and not germinated grains. Sinistrin is sparingly soluble in hot water, and separates on cooling as a turbidity; its solution is lævo-rotatory, while that of the sugar in barley, which is crystalline and does not reduce Fehling's solution, is dextro-rotatory. On account of the large quantity of sinistrin in fresh barley, its infusion is left-handed, while that of malt is right-handed. Barley contains also a soluble proteid, and one which coagulates. C. S.

Vegetation of Maize commenced in an Atmosphere Free from Carbonic Anhydride. By M. BOUSSINGAULT (*Ann. Chim. Phys.* [5], viii, 433—443).—In a bottle of 10 litres' capacity, containing air deprived of carbonic anhydride, and a layer of silicious sand which had been washed, ignited, and then moistened with boiled distilled water, two grains of maize, weighing together 0.846 gram, were sown. Two other grains from the same source were analysed, and from the results the composition of the two which were sown was calculated. After 45 clear days, the two which were sown had developed into plants, the stalks of which were 24 centimeters high, and each had three well-formed leaves, and a fourth just forming. At this stage, this portion of the experiment was stopped. Of the grains, nothing but the empty skins remained, the starch, albumin, and fat which had filled the cells had been modified or burnt by a sort of respiratory combustion, and on one of the products, viz., carbonic anhydride, the leaves provided with chlorophyll had acted, in order to re-instate the carbon in the body of the organism which they create with the assistance of light.

This clearly establishes the chemical composition of the harvest with regard to the composition of the seeds.

The plants, which weighed 0.6894 gram, when dried, were analysed; the results are compared with the composition of the dried grains, thus:—

		Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.
Grains . . .	0.7428	0.3303	0.0473	0.3404	0.0114	0.0134
Plants . . .	0.6894	0.3046	0.0487	0.3109	0.0114	0.0138
Differences	-0.0534	-0.0257	+0.0014	0.0295	-0.0000	+0.0004

During the vegetation there was, therefore, a loss of matter; the loss in carbon must have remained as carbonic anhydride in the bottle. The experiment clearly demonstrates that a seed placed in a sterile soil, surmounted by a sterile atmosphere, develops at first, in germinating a fertile, that is to say, a carboniferous atmosphere, in the midst of which the leaves, by the aid of light, produce chlorophyll, and afterwards amylaceous and saccharine substances. It has been established

by the observations of eminent physiologists, that leaves containing granules of chlorophyll, when exposed to light in presence of carbonic anhydride and water, give rise to the formation of starch, sugar, and similar bodies, at the same time evolving oxygen.

The presence or absence of green protoplasm establishes, therefore, two orders of cellules; those which introduce matter into the organism, and those which do not, but in which the principles formed by the action of the chlorophyll and light, as well as the albuminoids, undergo great modification, whether by oxidation or by the intervention of diastatic ferments. The changes effected in the vegetable cells which are without chlorophyll, may even occur in the epidermic cells, and in the fluids of the animal kingdom. These substances, apparently, proceed from the principles formed in the leaf and in a cellule without chlorophyll; in an animal cellule, saccharose may become invert sugar, starch a fatty body, &c.; but these cellules cannot create either of those substances, creation being understood to mean the faculty of introducing into the economy, things which vegetate or which breathe, inert elements taken from the air, water, or earth.

This principle has been announced by M. Dumas and the author, thus: "Animals do not create; they simply transform the principles elaborated by plants."

The inferior order of plants which do exist without chlorophyll or light, do not possess the power of dissociating carbonic anhydride; they draw their carbon from other more highly-organised bodies; either living or dead, which had been thus highly organised by the action of chlorophyll and light.

C. H. P.

Analysis of the Ash of the Ground Pea (*Arachis Hypogæa*) as cultivated in Virginia. By WILLIAM S. BROWN (*Chem. News*, xxxiv, 147—149).—In 100 parts of pure ash, excluding ferric oxide, which the authors believe to be an accidental impurity, there were found:—

	Root.	Stem.	Leaves.	Husk.	Seed.
K ₂ O.....	23.043	25.902	15.880	37.395	37.134
Na ₂ O	18.816	3.063	2.897	3.763	3.342
CaO	28.180	43.440	53.712	20.145	3.749
MgO	8.706	13.296	4.844	13.506	14.262
P ₂ O ₅	3.684	1.590	4.679	5.062	29.102
SO ₃	13.015	10.613	15.235	17.749	11.742
Cl	1.162	1.501	2.533	0.486	0.346
SiO ₂	3.705	0.983	0.791	2.003	0.401
	100.261	100.338	100.571	100.109	100.078
Deduct O equivalent to Cl..	0.261	0.338	0.571	0.109	0.078
	100.000	100.000	100.000	100.000	100.000

In the dried plant the ash is as follows:—

Root.	Stem.	Leaves.	Husk.
11.830	13.288	7.747	2.586

Oil = 47.34 per cent.

Nitrogen = 3.415 per cent.

W. R.

Comparative Analysis of Roots of Vines. By M. BOUTIN (*Compt. rend.*, lxxxiii, 735—740).—The author finds that in American vines which have resisted the attacks of the phylloxera, a resinous principle exists in the roots, especially in their bark, and that it is present in about double the proportion in which it occurs in the French vines. He believes that the resisting power of the American vines is due to this resinous body. The puncture made by the insect is cicatrized by the exudation of the resinous matter, when this is present in sufficient quantity, and the escape of the nutritive juices of the plant is thus prevented. The nodosities which the insect causes do, in fact, disappear after a time, and a root-fibre is sent out from the spot where the bark has been wounded. R. R.

Alcoholic Fermentation. By A. FITZ (*Deut. Chem. Ges. Ber.*, ix, 1352—1355).—Pure *Mucor racemosus* grows in a solution of milk-sugar without producing fermentation or inverting the sugar; but on inverting it by an acid, the fungus acts as ferment. *Mucor racemosus* does also not produce fermentation in a solution of inulin, but readily in levulose prepared from it.

When *Mucor racemosus* is added to must of different percentage of glucose, fermentation easily sets in at 25—30°, but ceases as soon as 2.5 per cent. of alcohol is formed, while the action of *Mucor mucedo* ceases when the liquid contains 0.5 per cent. C. S.

Fermentation of Glycerin. By A. FITZ (*Deut. Chem. Ges. Ber.*, ix, 1348—1352).—Redtenbacher found that when a mixture of glycerin, water, and yeast ferments, it yields acetic and propionic acids, and Berthelot obtained alcohol by fermenting a solution of glycerin with chalk and casein.

The author obtained quite different results by using a mixture of 2000 water, 100 glycerin, 1 potassium phosphate, 0.5 magnesium sulphate, 2 German pepsin, and 20 chalk, to which was added a trace of a schizomyceta, which will be described in a future communication. At a temperature of 40° the liquid soon begins to ferment, carbon dioxide and hydrogen being given off, and the fermentation is finished in ten days. The solution then contains *normal butyl alcohol* and *normal butyric acid*, besides a little ethyl alcohol, and a higher acid, probably caproic. 100 parts of glycerin yielded 7.7 pure butyl alcohol and 12.3 anhydrous calcium butyrate. C. S.

Analytical Chemistry.

Several Methods of Chemical Analysis. By H. PELLET (*Bull. Soc. Chim.* [2], xxii, 246—261).—1st. *Estimation of Chlorine in presence of Phosphoric Acid by Silver Nitrate and Potassium Chromate.*—The liquid in which chlorine is to be estimated is rendered neutral with calcium carbonate, after acidification with nitric acid. The determination is

then conducted as usual, potassium chromate being used as indicator. Organic substances, such as sugar, need not be removed. A correction must be made, owing to the solubility of silver chromate, by adding a few drops of potassium chromate to a quantity of distilled water equal in volume to that in which the silver has been estimated, and adding silver nitrate till a reddish colour is produced.

2nd. *Estimation of Ammonia in Salts of Ammonium.*—10 grams. of the ammonium salt are weighed out, and dissolved in 30 or 40 c.c. of water. After solution a few decigrams of pure calcium carbonate are added. The liquid is made up to 100 c.c. and filtered. The standard soda is prepared so that 50 c.c. correspond to 0.3 gram of nitrogen, and to 30 c.c. of dilute sulphuric acid, also representing 0.3 gram of nitrogen. The soda is added in excess, and the solution is boiled till all ammonia is expelled. The excess of soda is then estimated with the standard acid.

3rd. *Estimation of Lead, Barium, and Bismuth with Potassium Dichromate.*—The author's process differs from that of Mohr by the addition of an excess of bichrome, and by the estimation of the unreduced portion with salts of iron and potassium permanganate. He uses this method to avoid the removal of drops for the purpose of ascertaining the end of the reaction, and also because the usual test for excess of bichrome with silver nitrate does not give trustworthy results: for barium chromate reacts on silver nitrate when they are left long in contact.

4th. *Estimation of soluble Sulphates with Standard Solutions.*—The sulphuric acid is precipitated with excess of barium chloride; the excess of barium chloride is precipitated with excess of potassium dichromate; and finally the excess of the latter salt is determined by addition of excess of a ferrous salt, and titration with permanganate. The precautions to be observed are: the solutions must be neutral; if they are acid, calcium carbonate is used to neutralise them. If calcium sulphate is present in solution, the calcium is precipitated as oxalate, and the excess of oxalic acid thrown down with calcium carbonate. If nitric acid is present, its quantity is estimated with a ferrous salt and permanganate, and deducted from the final amount of permanganate required. If the liquid contains phosphoric acid, a few drops of calcium chloride are added, after neutralisation with calcium carbonate.

5th. *Estimation of the total Nitrogen in Manures, Soils, and various products of Sugar Works.*—The essential characteristic of the process is to mix the organic substance, if necessary, with an excess of starch or sugar, in order to reduce the nitrogen existing as nitric acid, or as nitro-compounds, to nitrogen, when the analysis is made by combustion with soda-lime. The author got good results in analysing nitro-stearic acid by this process.

6th. *Application of Pelouze's Process to the estimation of small quantities of Nitric Acid.*—Four white glass flasks, each capable of containing about 250 c.c., are taken. Introduce into No. 1 30 c.c. of hydrochloric acid, into Nos. 2, 3, and 4, 30 c.c. of hydrochloric acid, + 1 c.c. of a solution of ammonio-ferrous sulphate, containing 2 grams per litre, and 50 c.c. of hydrochloric acid. Boil all four. Nos. 2, 3, and 4 are slightly coloured,

owing to oxidation of the iron salt. No. 2 is approximately decolorised by adding a few drops of a solution of stannous chloride containing about 1 gram per litre, and 50 c.c. of hydrochloric acid (to be kept under a layer of olive oil). The same volume is added to Nos. 3 and 4, 2 c.c. of a solution of potassium nitrate, 0.001 gram = 1.000534 gram of nitric acid are added to No. 3, and to No. 4, 1, 5, or 16 c.c. of the liquid to be tested. The four flasks are kept boiling for about a quarter of an hour. The volume of the liquid ought not to exceed a few cubic centimeters. An excess of hydrochloric acid is disadvantageous. To the first flask 100 c.c. of distilled water are added, and potassium permanganate (0.1 gram per litre) is added till the liquid acquires a rose colour. This amount has to be subtracted from that added to the other flasks. The second, third, and fourth flasks are also diluted with 100 c.c. of water, and permanganate is added till a coloration is apparent. By comparison between the third and fourth the amount of nitric acid is calculated. This method gives very accurate results, provided no substances oxidisable by nitric acid are present.

W. R.

On the use of Platinum in the Ultimate Analysis of Carbon Compounds. By F. KOPFER (*Deut. Chem. Ges. Ber.*, ix, 1377—1385).—This method has been described by the author on page 660 of the last volume. He has now simplified it, but the paper can be understood only by the help of drawings.

C. S.

Estimation of Nitrogen Tetroxide in Organic Substances. Chemical Composition of various Gun-cottons, &c.—By P. CHAMPION and H. PELLET (*Compt. rend.*, lxxxi, 707). Organic substances which contain nitrogen tetroxide are completely reduced, under certain conditions, by ferrous salts.

When the substance to be examined is not carried off by the vapour of water, the apparatus described by F. Jean (*Bull. Soc. Chim.*, 1876, ii, 10) may be employed. A flask of 250 c.c. capacity is fitted with a caoutchouc stopper, through which pass two tubes, one leading to a pneumatic trough, the other, a funnel-tube drawn to a point, is provided with a tap. The portion of this tube between the tap and the point is filled with distilled water. About 0.5 gram of the substance is introduced into the flask, with about 50 c.c. of water, and a few grams of iron-ammonia-alum; the flask is closed, and the contents boiled until all the air is removed. The point of the delivery-tube is placed under a graduated bell-jar, and the funnel filled with a mixture of sulphuric and hydrochloric acids, which is allowed to flow slowly into the flask. The sulphuric acid is simply to assist in the decomposition of the nitro-body. When about 50 c.c. of the mixed acids have been introduced, the tap is closed and the boiling continued so long as gas is evolved. Subsequently the volume of the gas is read off, and the nitrogen calculated from the formula for the decomposition of nitrates.

For substances such as nitroglycerin, which are volatile in the vapour of water, the following method is adopted.

The strength of a solution of potassium permanganate is determined

by means of ferrous sulphate which has been heated to boiling, and decolorised by stannous chloride after acidification with hydrochloric acid. A measured bulk of the iron solution is then placed in a flask, decolorised as before, and cooled in a current of carbonic anhydride or after covering its surface with some petroleum oil. About 0.5 gram of the substance is then introduced, and the flask heated on a water-bath. When the substance is completely decomposed, the liquid is heated to boiling to remove nitric oxide, and titrated with the permanganate.

Abel's compressed gun-cotton, Russian collodion, and gun-cotton prepared by the authors, were all found to have a composition corresponding with the penta-nitrocellulose of Pelouze, and not the tri-nitrocellulose of Abel. A sample of gun-paper contained only two equivalents of nitrogen tetroxide. C. H. P.

General Method of Analysis of Vegetable Tissues. By E. FRÉMY (*Compt. rend.*, lxxxiii, 1136).—Up to the present time but little interest has been taken in the chemical study of vegetable tissues, and no general method, such as is used in mineral analysis, has been applied to their separation and estimation.

The following bodies have been distinguished in the principal tissues of vegetables: *cellulose bodies* (cellulose, paracellulose, metacellulose), *vasculose*, *cutose*, *pectose*, *calcium pectate*, *nitrogenous substances*, and various mineral compounds.

Cellulose Bodies.—In this class are included those bodies which dissolve without coloration in bihydrated sulphuric acid ($\text{SO}_4\text{H}_2 + \text{H}_2\text{O}$), producing dextrin and sugar, which are not sensibly altered by alkaline solutions, and resist for a long time the action of strong oxidisers.

The author has distinguished, by means of the ammonio-cupric reagent, three varieties of cellulose.

(1.) *Cellulose*, which dissolves immediately in the cupric reagent, and forms a large part of cotton and of the utricular tissue of certain fruits.

(2.) *Paracellulose*, which does not dissolve in the cupric reagent until after the action of acids; it forms the utricular tissue of certain roots and the epidermis of leaves.

(3.) *Metacellulose* (fungin).—Insoluble in the cupric reagent even after the action of acids; it is found chiefly in agarics and lichens.

In the analysis of vegetable tissue, the first variety of cellulose is determined directly by means of the cupric reagent; the second in the same after being submitted to the action of acids, and the third is dissolved in bihydrated sulphuric acid. When it is not required to distinguish these three bodies, the whole may be dissolved in the sulphuric acid.

Vasculose.—This substance constitutes the larger part of the ducts and spiral vessels; it generally accompanies cellulose in vegetables, but differs completely from it in composition and properties. It contains more carbon and less hydrogen than cellulose; and it is vasculose which cements the fibres and cells together.

It may be said to form the heavy part of woody tissue; it abounds

in hard wood and in the stony concretions of pears; the shells of nuts and the stones of apricots contain more than half their weight of vasculose.

Vasculose is insoluble in sulphuric acid, and in the ammonio-cupric reagent, also in alkalis under ordinary circumstances, but when heated with alkalis under pressure, it dissolves easily; it also dissolves in oxidising agents. Vasculose can be separated from cellulose by sulphuric acid or by the cupric reagent; but if it is intended to weigh the cellulose, the vasculose must be dissolved in dilute nitric acid.

Cutose constitutes the fine transparent membrane which covers the exposed parts of vegetables.

Cutose is insoluble in sulphuric acid, but dissolves in dilute solutions of the carbonates of potassium and sodium; with nitric acid it produces suberic acid. It is separated from cellulose by the cupric reagent, and from vasculose by potash at the ordinary pressure.

Pectose is insoluble in water, but is rendered soluble and transformed into pectin by dilute acids. It occurs in the utricular tissues of fruits and roots, and is estimated by heating with dilute hydrochloric acid, dissolving in water, and precipitating with alcohol.

Calcium pectate forms part of the membrane which binds the cells together. It is estimated by treatment with dilute hydrochloric acid, which liberates pectic acid in the insoluble state; this is dissolved in potash and reprecipitated by an acid.

The nitrogenous bodies and the inorganic constituents are determined in the usual way.

The following is a summary of the method of analysis.

Cold dilute hydrochloric acid decomposes the calcium pectate, setting free the pectic acid, which is weighed as alkaline pectate.

Boiling dilute hydrochloric acid changes the pectose into pectin, which is precipitated with alcohol.

The ammonio-cupric reagent dissolves the cellulose. Hot hydrochloric acid renders paracellulose soluble in the cupric reagent.

Sulphuric acid (bihydrated) dissolves the cellulose bodies.

Hot dilute potash dissolves the cutose.

Potash under pressure dissolves vasculose.

Dilute nitric acid renders vasculose soluble in alkaline solutions.

C. W. W.

Proximate Composition of Coal-gas. By W. DITTMAR (*Chem. News*, xxxiv, 145).—In a late memoir "Sur le Gas d'Eclairage," published by Berthelot and abstracted in this Journal (1876, ii, 183), he gave an analysis of the coal-gas of Paris, showing it to contain 3 to 3.5 per cent. of benzene, 0.1 of acetylene, 0.1 to 0.2 of ethene, and 0.02 of propene and other hydrocarbons, the remainder consisting of diluent, non-luminous gases. Unless the Paris gas has an exceptional constitution, this analysis throws discredit on all former analysts. Berthelot in fact accuses them of manipulating the figures they obtained in eudiometric determinations, so as to fit the hypothesis that the real illuminating principle of gas is ethene. The author disproves this accusation by adducing an analysis of gas by Bunsen, and shows

that what he states to be ethene could not have contained more than 17 per cent. of benzene.

The author made a series of experiments on Glasgow coal-gas, with the view of ascertaining how far his analyses would tally with those of the Paris gas of Berthelot. The gas was passed first through a long column of nitric acid of 1.5 specific gravity, and its illuminating power compared with that of the original gas. The gas was feebly luminous: hence it was inferred that olefines were not absent in an exceptional degree. To reassure himself on this point, the author prepared mixtures of ethene with hydrogen, and on testing their illuminating powers, he found that a mixture of 3 volumes of hydrogen to 1 volume of ethene was sufficient to reduce its luminosity to that of marsh-gas, and a 10 per cent. ethene flame gave no more light than that of a Bunsen lamp; but a 3 per cent. benzene flame was sufficiently luminous. This argues in favour of Berthelot's theory. Yet considering the process of purification to which coal-gas is subjected, very little benzene can remain in the gas: for a 6 per cent. mixture of benzene vapour with hydrogen, after being shaken with water, was found to have the proportion of benzene reduced to 2.

The author failed in his attempts to separate benzene from olefines. Nitric acid of 1.4 or 1.5 sp. gr. is not the proper means of separation, for it acts on ethene as well as on benzene. Non-vulcanised india-rubber gave the best result. A trial was accordingly made to separate these hydrocarbons from each other by its use; the gas, after being dried over calcium chloride, was passed over a coil of sheet india-rubber, and condensed in bromine. The resulting bromide boiled below the boiling point of propene bromide (142°). The percentage of bromine was 83.52, hence assuming the formula of the bromide as $C_nH_{2n}Br_2$, the result is:—

$$C_nH_{2n} = 31.6; C_2H_4 = 28; C_3H_6 = 42.$$

With alcoholic potash more than half the bromine was removed, showing that it did not consist of monobromobenzene, but of bromides of the olefines. The author therefore disputes the accuracy of Berthelot's statement.

W. R.

Detection of Alum in Bread and Flour. By J. A. WANKLYN (*Analyst*, 1876, 14).—As flour contains gluten—a substance containing about 1 per cent. of sulphur—sulphuric acid always appears in the ash of flour and bread. Sulphuric acid added in the form of alum may probably be found in the cold aqueous extract of the flour; before determining the amount of sulphuric acid, the soluble gluten must be coagulated and removed.

M. M. P. M.

Estimation of Colour in Water. By C. A. CAMERON (*Chem. News*, xxxiv, 77).—Although it has been proposed to use solutions of caramel instead of standard solutions of ammonia for the purpose of comparison in "Nesslerising" water, the author does not recommend the use of the former solution, as even when it contains much alcohol, it becomes turbid and useless after a time, and soon changes its hue.

To those who prefer caramel solutions the use of coloured discs of the following description would be more favourable. Fill a Nessler tube with distilled water, and place it over a disc so coloured that, on looking down through the column of water, it may, by the reflected light from the disc, have the colour of a solution of say 0.005 gr. of ammonia per gallon of water mixed with the usual 4 per cent. of Nessler's solution. A dozen discs would be sufficient, but in using them the Nessler's solution should be always of exactly the same composition. D. B.

Anthracene Testing. By J. T. BROWN (*Chem. News*, xxxiv, 136).—In applying the anthraquinone test to commercial samples of anthracene, various minor difficulties occur; one of which is that damp samples are apt to lose moisture during the time occupied in reducing them to a sufficient degree of fineness to allow the small quantity of 1 gram to be a correct sample of the bulk, while another and more serious difficulty is the uncertainty caused by the occasional occurrence of accidental impurities in the quantity weighed out. To obviate these difficulties, the author proposes the following modification of the test:—50 grams of the crude anthracene are weighed out, and 250 c.c. of petroleum spirit measured out; the anthracene is triturated in a mortar with a sufficient quantity of the spirit to form a thin cream, which is poured into a weighed filter (retaining any grit or sand) and washed with the remainder of the spirit. The residue having been drained, the filter is carefully folded, pressed between bibulous paper, dried at about 60–80°, and weighed. The contents of the filter are crushed to a fine powder, one gram of which is weighed out and treated by the ordinary anthraquinone test. D. B.

Note by the Abstractor.—The above-mentioned modification is of but little importance with regard to the commercial mode of testing anthracene, as the temperature at which trituration takes place, and the density of the spirit used, materially influence the results obtained, besides which petroleum spirit does not remove hydrocarbons of a boiling point approaching near that of anthracene. D. B.

An Abnormal Sample of New Milk. By J. PATTINSON (*Analyst*, 1876, 47–50).—The milk was obtained from a roan cow pronounced to be in good health; no salt was given as such in the food: the farm was situated not far from the sea. The following are the results:—

	Milk from roan cow.	Milk from white cow, near roan.	Average milk from 8 cows in stable.
Water.....	90.15	86.80	87.54
Fat	3.00	3.71	3.53
Casein.....	2.00	3.97	3.05
Milk sugar.....	3.90	4.65	3.15
Ash.....	0.95	0.87	0.73
	100.00	100.00	100.00
Chlorine in ash....	0.27	0.14	0.13
Equal to sodium chloride	0.44	0.23	0.21
			M. M. P. M.

Analysis of Butter. By J. MUTER (*Analyst*, 1876, 7—14).—Pure butter always contains a notable amount of fatty acids other than palmitic, oleic, and their congeners. The author's process is as follows:—(1.) Water is estimated by drying 100 grams over a low gas-flame at 110° till effervescence ceases, and the curd and salt sink to the bottom, leaving the butter-fat perfectly clear. (2.) The melted fat is poured off into a beaker, the residue decanted on to a weighed filter, washed with petroleum-spirit, dried, and weighed as curd and ash. (3.) The filter is ignited: the ash is reported as salt. (4.) The fat poured off in (2) is filtered—if not perfectly clear—and brought into a specific gravity bottle fitted with a thermometer stopper: the bottle is placed in water maintained at 39.5° (103° F.), the fat being itself at 35° (95° F.) when it is transferred to the bottle: the water surrounding the bottle is allowed to cool until it reaches 37.7° (100° F.), when the bottle is withdrawn from the hot water, dried, and weighed. This experiment is repeated three times. The quantity of water at 37.7° (100° F.), which the bottle contains, has been already determined. The specific gravity of the fat at 37.7° is then obtained, referred to water at the same temperature.

(5.) About 10 grams of the fat at 37.7° are weighed into a clean dry 800—900 cb.c. flask; 0.3 gram caustic potash and 60 cb.c. rectified spirit are added. The flask is placed in boiling water and maintained at this temperature until no turbidity ensues when water is added. 500 or 600 cb.c. of water is added and heating continued, until the whole of the alcohol is evaporated. The contents of the flask are made up to about 400 cb.c., with nearly boiling water; a cork carrying a tube 2 feet long is placed in the mouth of the flask; and 5 grams of strong sulphuric acid is poured down the tube, followed by a little water. The flask is agitated with a circular motion until the fatty acids rise as a clear stratum, which, by cooling to 3° or 4° , solidifies to a cake. The cork is removed, a piece of cambric is fastened over the mouth of the flask, and the liquid is decanted (without breaking the cake) into a litre flask. After washing with a little cold water, 300—400 cb.c. of warm water are added, the cork of the tube is inserted, and the whole is heated to about 75° , the contents being agitated until the fat forms an emulsion with the water; the contents are then cooled, the water decanted through cambric, and this process is repeated until the washings are perfectly free from acid. The flask is now dried until the fats are fused, when they are poured into a platinum basin and weighed. Any fat adhering to the flask is dissolved in a little ether, which is evaporated in a small weighed beaker; the cambric is also, if necessary, exhausted with ether. The filtrate is made up to 1 litre; the total free acid is estimated in a portion by standard soda and calculated as H_2SO_4 ; 100 cb.c. are precipitated by barium chloride, and from this total H_2SO_4 is calculated. Another portion is evaporated to dryness; the residue is heated in a covered platinum dish till fumes cease; a fragment of ammonium carbonate is added; and the whole again heated. The K_2SO_4 so found is calculated to H_2SO_4 , which is noted as combined sulphuric acid. From these data the free sulphuric is obtained, which, deducted from total free acidity, gives free acid other than sulphuric, in solution: this is calculated to butyric acid.

The author adopts 88 per cent. of fatty insoluble acids as a standard for calculation, if associated with at least 6·3 per cent. of soluble acids. but would not consider a butter adulterated if it showed less than 89·5 per cent. insoluble, and 5 per cent. soluble fatty acids.

There is an invariable relationship existing between specific gravity at 100° F., and of most of acids. M. M. P. M.

Detection of Colouring Matters in Wine. By A. DUPRÉ (*Analyst*, 1876, 26).—This paper describes a method for detecting the presence of the colouring-matters of logwood, brazil-wood, and cochineal in wine. These substances dialyse; the colouring-matter of pure red wines does not. (Certain artificial colouring-matters—rhatany-root, for instance—do not dialyse.) If the dialysate obtained from a red wine is yellow or brownish-yellow, it is to be examined chemically and optically. Logwood and Brazil-wood alter so much with age that the only safe method is to keep a tincture of known age for comparison. The ammoniacal solution of cochineal colouring-matter yields these well-marked absorption-bands. M. M. P. M.

Detection of Fuchsine in Wine. By E. BOUILLON (*Compt. rend.*, lxxxiii, 858—859).—Instead of using potash or ammonia, the author employs baryta to liberate the rosaniline of the fuchsine, sometimes used in fraudulent coloration of wines. 500 cb.c. are evaporated in a basin to about 125 cb.c., the heat is removed, and 20 grams of barium hydrate are added. The mixture is shaken, allowed to cool, and filtered, and the filtrate is made up to 125 cb.c. with distilled water. A few crystals of baryta must now be added to make sure that all the colouring-matter of the wine is precipitated. It is then shaken with 50 or 60 cb.c. of ether; the layer of ether is decanted into a basin; one drop of acetic acid of 8°, and three or four drops of water are added; and a small piece of white silk. If an appreciable amount of fuchsine is present, the silk assumes a pink colour immediately; if not, the ether must be allowed to evaporate; the few drops of water remaining are evaporated nearly to dryness; and the silk is again dipped in the liquid. This process allows the detection of one hundred millionth part of fushsine in wine. W. R.

Technical Chemistry.

Composition of Ancient Glass and Crystal. By E. PELIGOT (*Compt. rend.*, lxxxiii, 1129).—The following results were obtained from various specimens of ancient glass analysed by the author:—

SiO ₂	66·7	66·0	67·4	70·9	69·4	69·4
CaO	5·8	7·2	2·7	7·9	6·4	7·1
Al ₂ O ₃ , Fe ₂ O ₃ and MnO ₂	2·8	3·0	5·4	4·5	2·9	2·8
K ₂ O and Na ₂ O	24·7	23·8	24·5	16·7	21·3	20·7

100·0 100·0 100·0 100·0 100·0 100·0

Soda and potash generally occurred together, showing that the alkali was obtained from the ashes of marine plants. The proportion of lime was only the half or the third of that now in use, the consequence of which was that the glass generally altered considerably on exposure to the air.

A specimen of glass, of which one cubic inch weighed 1600 grains, contained nearly one-half of its weight of lead oxide. C. W. W.

Presence of Copper in Cast-iron. By S. KERN (*Chem. News*, xxxiv, 78).—Wrought-iron containing some tenths per cent. of copper is known to be red-short; nevertheless, some of the best irons from Siberia have been found to contain from 0.01 to 0.03 per cent. of copper. Some specimens of steel contained 0.2 per cent., the steel was not brittle, and had been used with success for the manufacture of steel axles. Specimens of cast-iron from blast furnaces of the South Ural mountains showed, when examined and analysed, that the presence of copper in cast-iron may amount to a higher percentage than in steel or iron without altering the quality of the metal. The following is the composition of this peculiar sample of cast-iron:—

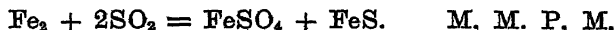
Fe.	Cu.	Sn.	CO.	Si.	Ni.	C.	Mn.	
83.514	8.123	1.252	0.501	0.952	0.125	3.001	2.312	= 99.780.

For detecting mere traces of copper, the author used the following method:—The specimen is dissolved in hydrochloric acid, and the copper and iron are precipitated by an excess of ammonia; the mixture is boiled and filtered, the blue liquor evaporated nearly to dryness, and the resulting residue is dissolved in sulphuric acid. In this solution a piece of magnesium ribbon is placed, which, if traces of copper are present, is quickly covered with a layer of that metal easily observed under the microscope. D. B.

Stove-pipe Deposit. By S. D. CRENSHAW (*Chem. News*, xxxiv, 190).—A thick orange-yellow liquid mass was observed trickling down from the joints of the pipe of a stove burning Pennsylvania anthracite. This substance was found to consist of:—

(NH ₄) ₂ SO ₄	FeSO ₄	H ₂ SO ₄	S.	C.	H combined with C.	Cl	SiO ₂	H ₂ O	
80.48	3.73	0.64	7.35	1.34	0.11	trace	0.12	0.23	= 94.*

The free sulphur is perhaps produced by the action of the iron of the pipe upon sulphur dioxide at a low temperature,



Preparation of some Coloured Fires used in Pyrotechny. By S. KERN (*Chem. News*, xxxiv, 139).—The following tables of coloured fires (red, green, and violet) were worked out by the author to show the quickness of burning of coloured fires, since in some cases, as decorations and lances, they must burn slowly, in other

* There must be a mistake here: the sum is given as 100, but the percentage amounts only add up to 94.—(M. M. P. M.)

cases as wheels, stars for rockets, and Roman candles, they must burn more quickly :—

Green fires.				Red fires.				Violet fires.			
No.	Potassium chlorate.	Barium nitrate.	Sulphur.	Potassium chlorate.	Strontium nitrate.	Sulphur.	Carbon powder.	Potassium chlorate.	Calcium carbonate.	Malachite, powdered.	Sulphur.
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
1..	36	40	24	40	39	18	3	52	29	4	15
2..	29	48	23	32	46	19	2	52	28	5	15
3..	24	53	23	27	51	20	2	52	26	7	15
4..	21	57	22	23	55	20	2	52	24	9	15
5..	18	60	22	20	58	20·5	1·5	52	23	10	15
6..	16	62	22	18	60	21	1	52	21	13	15
7..	14	64	22	16	61·6	21·2	1·2	51	20	14	15
8..	13	66	21	15	63	21	1	51	18	16	15
9..	12	67	21	13	64	22	1	51	16	18	15
10..	11	68	21	12	65	22	1	51	15	19	15
11..	10	69	21	11	66	22	1	51	13	21	15
12..	9·5	69·5	21	10	67	22	1	51	11	23	15
13..	9	70	21	10	67·25	22	0·75	51	10	24	15
14..	8·5	70·5	21	9·25	68	22	0·75	51	8	26	15
15..	8	71	21	9	68·35	22	0·75	51	6	28	15

No. 5 burns more quickly than No. 6 and more slowly than No. 4, &c. D. B.

Mode of Generating Sulphurous Acid for use as a Disinfectant. By T. W. KEATES (*Chem. News*, xxiv, 245—246).—The ordinary method of generating this gas by burning sulphur is cumbersome and very uncertain, owing to the difficulty of keeping up the combustion. The evolution of the gas from its solution in water is scarcely more convenient, and much less effective; and at present there is no ready, convenient, and easily controllable way of producing this valuable agent, whose action as a disinfectant is more powerful than that of any other preservative or purifying agent.

The author proposes the use of carbon bisulphide, which he introduces into an ordinary spirit lamp, and either burns alone or mixed with hydrocarbon liquids, such as petroleum. Sulphurous acid generated in this manner can be applied with facility to the disinfection of any place or object. In a room containing about 1,300 cubic feet of air, it was found that by burning 280 grains of bisulphide of carbon, the atmosphere was so charged with the gas that it was impossible to remain in the room for more than a few seconds. D. B.

On the Temperature required in Leblanc's Soda-process, and the Composition of the Gases Evolved. By F. FISCHER (*Deut. Chem. Ges. Ber.*, ix, 1558—1559).—The results are given in the following table :—

Time.	CO ₂ .	CO.	O.	N.	Temp.	Remarks.
h. m.						
9 10	16.9	—	5.1	78.0		
9 30	9.3	—	12.6	78.1	—	Five minutes after newly charging, door open.
9 40	14.5	—	6.9	78.6	—	Door shut.
9 50	14.7	—	6.9	78.4		
10 3	17.6	—	5.7	76.7	—	Charged stirred up at 9.53 and 10.
10 12	16.7	—	5.7	77.6		
10 25	14.3	—	7.3	78.4		
10 45	—	—	—	—	713°	Fresh charge at 10.35.
10 55	15.7	—	5.3	79.0		
11 15	18.1	—	3.3	78.6	779°	
11 30	—	—	—	—	874°	
11 45	15.8	—	6.1	78.1	932°	Ten minutes after stirring and just before drawing the charge.
12 28	13.1	—	9.0	77.9	—	Ten minutes after charging.
12 36	15.3	—	5.8	78.9		
12 55	11.3	—	11.0	77.7		
1 10	14.3	0.2	7.6	77.9	—	Directly after stirring the fire.
1 30	15.6	—	6.9	77.6	—	Ten minutes after stirring charge.
1 36	13.6	—	8.3	78.1		
1 45	8.3	—	12.5	79.2	—	Furnace empty.
2 0	14.8	—	6.2	79.0	—	Furnace freshly charged.

Charge of furnace—

150 kilos. sulphate.

160 „ limestone.

60 „ coal (9 per cent. of ash).

Produce 240 „

Quantity of coal used 96 kilograms.

G. T. A.

Alkali from Sea-weed. (*Chem. News*, xxxiv, 201.)—A concentrated solution of sea-weed ash is added to the liquor containing chlorides of sodium and calcium, left in the ammonia-soda process after the ammonia has been recovered by boiling with lime. The potassium, sodium, and magnesium sulphates in the sea-weed ash are decomposed, with precipitation of calcium and magnesium sulphates, in a form available for paper-making. The last traces of sulphates are precipitated by means of barium chloride solution. Iodine is then precipitated by means of lead nitrate; the liquid after filtration is boiled, and sodium nitrate is added, whereby chloride of potassium is converted into nitrate which crystallises out. The solution is then ready for treatment by the ordinary ammonia-soda process. It is proposed to work this process along with the ammonia-soda process now practised at Aalborg, in Jutland.

M. M. P. M.

Action of different Fatty Oils upon Copper. By Wm. THOMSON (*Chem. News*, xxxiv, 176, 200—213).—Strips of copper were immersed for ten months in various fatty oils. In the first series of experiments the copper was wholly, in the second partially immersed. A portion of the oil was then tested for copper, another portion was

warmed and shaken with water, and the water tested for copper and for acid. The general results were as follows:—

1. The amount of acid in the water bore no relation to the amount of copper dissolved by the oil.

2. When the quantity of copper dissolved was large, the quantity going into solution in the water was also generally large.

3. Certain oils caused the formation of a green sediment upon the copper; little or no copper was dissolved by these oils. No fish oil, except American sperm oil, produced a deposit on the copper.

The following oils produced sediments:—Series I. Olive; palm; palm-nut; foreign neatsfoot; English ditto; tallow. Series II. Olive; palm-nut; ground nut; American tallow; common tallow; lard. Pale and brown rapeseed produced deposits only at the point where the copper came into contact with the surface of the oil. American sperm produced a slight green deposit at the surface of the oil. North American neatsfoot covered the copper with a network of green deposit.

The following oils dissolved much copper, without causing any deposits:—Series I. Refined rape; linseed; raw cod-liver; Newfoundland cod; common seal. Series II. Pale rape; American sperm; pale seal. Brown rape, castor, raw linseed, and English neatsfoot tarnished the copper, and simultaneously dissolved large quantities of the metal.

The following oils dissolved smaller quantities of copper, without producing any deposits:—Seal; pale seal; whale; cod; shark; East Indian fish.

The following produced a dark-coloured deposit on the copper:—Series I. Non-refined rape; pale cotton-seed; ordinary cotton-seed; almond. Series II. Raw linseed; English neatsfoot; cotton-seed; brown rape. Three mineral oils produced in both series a greyish deposit. English neatsfoot and tallow alone in Series I, dissolved no copper. In Series II, one sample of olive, palm nut, American tallow, common tallow, and whale dissolved no copper.

The green deposit formed on the copper appears to contain a fatty acid; it is under examination. M. M. P. M.

Manufacture of large Castings of Nickel and Cobalt. (*Dingl. polyt. J.*, cccxii, 175—177.)—Winkler pointed out the difficulty with which large casts are prepared with the above metals, the chief objection to casts of that kind being that unless properly managed they will not be solid and free from blisters. For this purpose it was necessary (1) to produce a sufficiently high temperature; (2) to prepare fire-proof fusion vessels; (3) to avoid the presence of carbon and silicon in the fusing metals; and (4) to cast the mass in an atmosphere free from oxygen.

The fusion apparatus consisted of a round fire-proof oven, similar in construction to Deville's blast-furnace. The crucible was placed on an iron plate in the middle of the furnace, the latter filled with charcoal, and the whole heated to moderate redness. The coal and ash were removed, the oven cleaned out, and charged with a fresh quantity of charcoal. Air was then blown into the furnace from the cylinder of a blast-engine at the rate of 7 to 9 c.m. per minute, which resulted in a violent combustion, with production of a very high temperature. The

heat produced from charcoal alone was too transient, whereas with coke alone scorification was occasioned too quickly, so that it was necessary to change the fuel and to fuse the mass for five minutes with pure charcoal, for five minutes with 2 vols. of charcoal and 1 vol. of coke, for five minutes with 1 vol. of charcoal and 1 vol. of coke, and for five minutes more with pure coke. By observing this rule it was possible to obtain within twenty minutes a blue heat which was quite insufferable to the eye, and with which it was very easy to fuse 5 to 6 kilos. of cobalt or nickel. The crucible was taken out of the furnace after the fusion, the cover removed, and the metal in its dazzling hot state poured into forms made of dry sand or burnt clay. As the best English graphite crucibles would not resist the action of this very high temperature, other crucibles had to be prepared, and it was found most advantageous to prepare them from a combination of crucibles consisting of various materials. A Hessian clay crucible was placed in a graphite crucible, the interstice filled up with fire-clay, and a large crucible of Elgersburg porcelain embedded inside the clay crucible by a magnesia lining.

It was necessary that the covers of these crucibles should have the thickness of bricks. After the crucibles had been charged, the lids were fastened on by means of a mixture of burnt and unburnt porcelain clay and soluble glass, leaving only a very small outlet in the lid. The charge consisted in the first place of pure ignited powdered oxide of cobalt or nickel, which was intimately mixed with 10—12 per cent. of pure starch or wheat flour, and brought into a crucible. The latter was put inside another, and the space filled in with powdered charcoal. The crucibles were raised to a slight red heat, and cooled. The inner crucible now contained the cobalt or nickel in the form of a fine powder, which, with exception of being slightly carbonaceous, contained only traces of impurities. The cobalt mixture contained about 0.3 per cent. of nickel, and that of the nickel about 0.3 to 0.5 per cent. of cobalt. This fine metallic powder was then intimately mixed with 25—30 per cent. of its weight of pure oxide of cobalt or oxide of nickel, and the mixture heated in the above-described porcelain crucible. Thus the whole of the carbon present in the metallic mixture was burnt by the oxygen of the oxide, and the pure metal, together with excess of oxide added, was quickly brought into a state of perfect fusion.

During the casting the fluid metal often began to froth up and spirt when it was brought into the moulds and cooled. This was probably due to an absorption of oxygen, which the hot mass on cooling expelled suddenly. The resulting casts were not solid, but blistered. To remedy this defect the moulds were surrounded by a stout cotton wick which had been previously saturated with tar or petroleum. These were ignited as the hot metal approached the moulds, and formed a large reducing flame, through which the hot metal was passed. The castings were then allowed to cool slowly.

D. B.

On Anthracene Production. By FRED. VERSMANN (*Chem. News*, xxxiv, 211).—The manufacture of alizarin, although remunerative at first, has fallen very far short of the hopes which it incited, and

numerous failures have occurred amongst public companies as well as private firms engaged in it. These failures can be only partially attributed to the depressed condition of trade; the real cause is to be found in the unhealthy state of the anthracene manufacture, the excessive demand which sprang up some years ago having tempted many distillers to manufacture an article of very doubtful quality.

In 1877 there will be produced in England alone at least 1,400 tons of 100 per cent. anthracene. The requirement of all the alizarin works together does not exceed 600 tons of anthracene. This anthracene is, however, far from pure, for all solid hydrocarbons tested with alcohol and melting at 190° C. have been sold as anthracene. The prosperity of the alizarin manufacturers depends on their getting pure anthracene, and the tar-distiller will certainly find his advantage in producing it, since the demand for anthracene and the price of it will rise with the prosperity of the alizarin manufacture.

W. R.

Correction relative to a Communication on Panification in the United States, and the Properties of the Hop as a Ferment. By M. SACC (*Compt. rend.*, lxxxi, 361).—In a previous paper (*Compt. rend.*, lxxxi, for December, 1875), the author gave a process for the preparation of a fermenting agent to be employed in bread-making, which consisted of a decoction of hops mixed with beer yeast, made into a thick paste with corn-flour, and then rapidly dried and powdered. This powder, when kept dry, preserved its activity for any length of time, and for use was to be mixed with a little flour and water. In a few hours this would be in full fermentation, and ready for admixture with the dough for bread-making. The activity was at that time stated to be due to some principle in the hop, but it is now shown that the only function of the hop is to preserve the true yeast by preventing lactic fermentation.

C. H. P.

Injurious Character of Many Objects made of India-rubber. By B. TOLLENS (*Deut. Chem. Ges. Ber.*, ix, 1542).—Children's toys and the caps of feeding-bottles, etc., are often made of india-rubber containing zinc-oxide and other hurtful matters. The author found in a toy, which had produced sickness in a child who had been sucking it, 60.58 per cent. of zinc oxide, and in another, which was warranted as "harmless," 57.68 per cent., as well as traces of lead, iron, lime, and sand.

G. T. A.

On the Effect of Sewers, &c., on the Purity of the Soil. By GUSTAV WOLFFHÜGEL (*Zeitschr. f. Biologie*, xi, 459—482).—The effect of laying down large sewers in Munich was found to be that after a few years, the soil surrounding the sewers (previously strongly impregnated with drainage matters) became ameliorated, the amount of matters soluble in water, organic matters (loss on ignition), and nitrogen, becoming largely diminished.

Sewers when newly constructed, are, as might be expected, somewhat more porous and pervious to water than when they have been in use for some time.

C. R. A. W.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

VI.—*Observations on Fluid-cavities.*

By WALTER NOEL HARTLEY, F.R.S.E., King's College, London.

I. *On the probable Temperature incident to the Formation of Topaz.*

SINCE the publication of my last paper on the variations in the critical point of carbon dioxide in minerals, I have made an examination of the splendid collection of topazes in the British Museum. With the kind permission of Professor Storey-Maskelyne, I selected all those specimens which from their appearance were most likely to contain fluid cavities. The following were from the Ilmen Mountains, Ural:—

1. Colourless crystal of small size, with many cavities.
2. Colourless crystal, with cavities.
3. Colourless crystal of large size, full of fissures, very few cavities.

From Nertchinsk, Irkutsk, Siberia:—

4. Large crystal of slightly greenish-blue colour.

From the River Urulga, Nerchinsk, Irkutsk:—

5. A large crystal.

From Murchinsk:—

6. Blue topaz, piece of large crystal.

Each of these specimens contained cavities with a single fluid enclosed. This fluid was not affected by a temperature of 90° C., and hence was most probably water.

From Saxony:—

7. A yellow crystal.
8. The same.
9. The same.
10. The same.

Each of these specimens contained cavities with a single fluid therein. This fluid was unaffected at 90° C., and was most probably water.

Brazilian topazes, Minas Novas, Minas Geraes :—

11. }
12. }
13. } These were rounded pebbles. Two of them contained no flaw
14. } or blemish whatever. Any cavities noticed were empty.
15. }
16. A crystal. Contained what appeared to be water cavities only. From the nature of the specimen it was difficult to make a good observation.
17. A pebble split in two. Large cavities containing one liquid, apparently water, and a bubble which was at least half the size of the cavity.
18. A sliced specimen from New Holland, of a greenish tinge. Many large cavities with one liquid in each, which did not occupy quite one-half of the cavity. The liquid, for reasons already stated, was presumably water. About 1,000 cavities were examined in this specimen.

Cairngorms from Scotland :—

19. A polished slice, much fissured.
20. A magnificent crystal, cut and polished at one part. It contained what were apparently water cavities. These were few in number.
20. A slice off a large crystal, much fissured and full of cavities, many of large size. The slice contained liquid which appeared to be water. It occupied a little more than half the space in each cavity.

Topaz, a fluosilicate of aluminium ($\text{AlF}_3 \cdot \text{SiF}_4 \cdot 5\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), may possibly be formed, as Bischof has suggested, from the alteration of mica and felspar. The frequent association of topaz with granites in Brazil, in the Mourne Mountains, Ireland, with the decomposed granites of Scotland, and of the Ilmen Mountains, favours this view entirely. It is most probable that the process of conversion has been effected by the action either of alkaline fluorides or of cryolite on kaolin. In any such reaction no carbon dioxide would be liberated; hence we may not expect to find it very frequently in the liquid state in topazes, and when it does occur it may have been enclosed simply because it happened to be present, and not because it was a necessary product of the reaction by which the mineral was formed. At the time of its enclosure the water may have been in the vaporious state, and it is almost certain that the carbon dioxide was not liquefied, but in the condition of a highly compressed gas. That a high temperature pervaded the material at the time of its crystallisation is shown,

I think, by the fact which I have observed in some specimens, viz., that numbers of cavities, many of large size, were only half filled with a liquid which we have good reason to believe was water. The contraction of the water to one-half or less of the volume of the cavities' capacity is doubtless due either to condensation from the state of an enormously compressed vapour, or to contraction after cooling from a temperature approaching the critical point of water. In one and the same specimen of topaz I have noticed cavities containing very little, in fact a mere trace of water, and so much liquid carbon dioxide that the latter substance filled the cavities by expansion before the critical point of the substance had been reached. Let us call these cavities *a*. Side by side with these were cavities filled one-third by water, one-third by carbon dioxide liquid, and the remaining space by the same substance as gas; let these be denoted by *b*. The critical point, which was the same in all the cavities, 27.5°C. , shows that there is only a small amount of any incondensable gas present.

The contents of both cavities *a* and *b* must have endured the same pressure, which could not have been less than 109 atmospheres (tension of liquid CO_2 at $30.92^{\circ} = 109$ atmospheres, Andrews), and was probably very much greater. Now inasmuch as the carbon dioxide in the water cavity *b*, of which Fig. 1 is an example, is half gaseous and half liquid at the critical temperature 27.5° , and that in the cavities *a*, containing little water, is wholly liquid (in which the incondensable gas seems to dissolve, for it totally disappears when the liquid is expanded to the utmost), I conclude that the difference in the proportion of gas to liquid in *b* is due to the contraction of the water upon cooling. Any expansion of the crystal on the release of pressure it endured *in situ*, would have but slight effect on the capacities of the cavities, and may be disregarded. We do not know the rate of expansion of water at high temperatures, but between 4°C. and 100°C. it amounts to an increase of only 0.043109 in 1 volume (Kopp). The critical point of water, according to Cagniard de la Tour, is near the melting-point of zinc, or not lower than 342°C. (Daniell). No doubt the expansion of water would increase with great rapidity as the temperature approached its critical point. From these data I conclude that the temperature of the mineral at the time of formation was in all probability approaching the critical temperature of water. That the critical point was not attained I infer from there being so little water in the cavities *a*, for had such a temperature been attained, the mixture of gas and water vapour would have been uniform in composition, and a corresponding uniformity would have been noticed in the contents of the

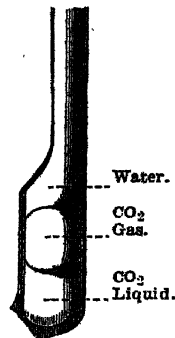


FIG. 1.

cavities. Although in the particular specimen to which I here make reference the temperature may have been below that at which water under any pressure assumes the condition of a vapour, yet in many other cases I am led to believe the temperature to have been above this point, on account of the small quantity of liquid present, thus in the topazes from Brazil, New Holland, and from Scotland (Nos. 17, 18, and 20).

Calculations necessitating a knowledge of the expansion of water at high temperatures, and the decrease in volume of its vapour by pressure when above its critical point, as well as the reduction in volume of incondensable gases at high pressures, must at present be little more than conjectures, since these are matters concerning which we require considerable additions to our present knowledge.

II. *An Examination of Rock Sections.*

A number of sections from the following rocks were cut for me and submitted to microscopical examination in the manner already described in one of my former communications: Basalt, from Samson's Ribs, Edinburgh; from Bolam, Durham; from Madeira. Volcanic breccia from Arthur's Seat, and gabbro from Corstorphine Hills, Edinburgh. Sections of the following granites: from Aberdeen, Peterhead, Tudyvan, Cornwall, St. Leven, Cornwall, Mount Sorrel, Leicestershire, the Mourne Mountains, Ireland, and Egyptian granite. Granitic porphyry from Altenburg, Saxony; quartz porphyry from Pwlheli, North Wales; porphyry from Royelle Bay, Jersey; Schorl granite from Luchons, Pyrenees; porphyry from the Chimney Rock, Penzance; and syenite from Guernsey.

Many of these specimens, in fact, almost all granites and porphyries, contained water cavities. These were found generally in the quartz, very seldom in the schorl, and scarcely ever in the felspar crystals. In some cases the cavities were very minute, and their contents barely distinguishable with a magnifying power of 800 diameters. Carbon dioxide appeared to be present in only two of these specimens, namely, in a granite from Cornwall, and in a specimen from the Mourne Mountains, but its occurrence is somewhat doubtful, as only one cavity in each section gave evidence of its presence. A specimen of felspar from near the summit of Snowdon, kindly lent to me by Mr. J. C. Young, F.G.S., contained in the quartz crystals a number of water cavities. In one of these, to which my attention was particularly directed by Mr. Young, there appeared to be no liquid; at least no bubble was seen; in a cold room, however, a moving bubble had been noticed.

By dropping a little ether on the slide it was sufficiently cooled by evaporation to allow of the liquid being seen. By immersion in iced water and hasty removal therefrom, the critical point was taken, or

rather what was the *apparent* critical point, namely the temperature at which the bubble disappeared; this, as I have shown already, is not necessarily identical with the true critical point. At 18° C. the bubble was plainly visible, and at 18·5° C. it had disappeared. The greatest diameter of this cavity was about $\frac{1}{80,000}$ of an inch, and at 0° C. the bubble had a diameter of about $\frac{1}{10,000}$ inch. Under certain conditions the bubble was kept in constant motion, but with regard to this fact I shall have further observations to make in a separate communication. I was at considerable pains to ascertain whether this liquid simply filled the cavity by expansion, or whether it attained its critical point at 18·5°. I found it had simply expanded. Previous to my having made this examination of rock sections, I was impressed with the idea that the depths of the earth contained carbon dioxide and water in superabundance, and that the enclosure of these substances was simply a matter of accident, and not immediately connected with the reaction or reactions resulting in the formation of the minerals. I therefore expected to find carbon dioxide of constant occurrence in rocks and minerals, for since little or no special search seems to have been made for it, it was quite likely that it might be contained in cavities of minute size, such as are seen in granites, &c., and have been regarded hitherto as water. I have now a decided inclination to believe that it occurs but rarely.

III. *On Gas-bubbles denser than Water.*

I have already pointed out (on variation in the critical point of carbon dioxide in mineral cavities, *Journal of the Chem. Soc.*, 1876, vol. ii, p. 237) that by compression a gas may be rendered denser than water. I have since obtained evidence of the existence of gases in a piece of rock-crystal so condensed that these conditions may easily be induced. The gas-bubbles float on a liquid, which I have proved to be water. By exposing the crystal to a uniform rise of temperature, the water is expanded and the gas compressed to such an extent that the bubbles sink and do not rise till after the liquid has sufficiently cooled.

It is here to be remarked that experiments made upon a hot stage which warms only one side of the cavity are apt to give fallacious results, and it is necessary to make use of a microscope with a revolving stage, so that the bubble may be moved about freely. It should be of such a size as to be plainly discernible with a 2-inch objective, and sufficiently mobile to act like the bubble in a spirit-level. The sinking and rising motion is slow, like the movement of a globule of oil in water. The supposition that the temperature causes the gas-bubble and the liquid to change their relative densities is favoured by the fact that when the specimen is cooled in iced water, a much higher temperature than usual is required to produce the effect. Then again

in large deep cavities the bubbles were seen to descend so far as to be entirely out of focus, and in order to bring them into view, the object-glass was made to approach the specimen; but when on cooling the bubbles returned to their original position, the objective had to be withdrawn. I desire particularly to point out that, as I have noticed other effects due to heat which might under certain conditions cause bubbles to move towards the lower ends of their cavities, great caution was taken to eliminate all circumstances which might lead to a wrong interpretation of facts, and some thousands of experiments were made on different cavities.



FIG. 2.

An account of the method of ascertaining the temperature at which the bubbles sink here follows. A cavity of regular shape in a specimen of rock-crystal (Fig. 2) which contained carbonic acid cavities, proved an exceedingly good one to operate upon. It contained but one liquid, water, and the bubble could be seen with a 2-inch objective moving about from point to point as the microscope stage was rotated. Preliminary trials with a hot spatula

showed that in whatever position the cavity was placed the bubble always sank by rise of temperature.

The specimen was then detached from the glass and mounted between pieces of stout sheet platinum. The microscope was in a horizontal position, so that the specimen hung vertically. Mercury was heated in a platinum crucible, and the specimen, after being arranged in the focus of the instrument, and adjusted in such a manner that it could be instantly replaced, was removed and plunged into the hot mercury.

The following is a statement of the observations made in this way, and I am convinced that they may be depended on:—

Temperature.

1st Exp.	200° C.	The bubble had sunk into the lowest extremity, and was seen to return suddenly.
2nd Exp.	190	Bubble had sunk, but floated again on cooling.
3rd Exp.	180	The same.
4th Exp.	160	The same.
5th Exp.	150	The same.
6th Exp.	140	The bubble had not changed its position.
7th Exp.	145	The bubble had not moved.

	Temperature.	
8th Exp.	150° C.	The bubble had not moved.
9th Exp.	150	The bubble had sunk.

On this last occasion the bubble did not quite resume its original position on cooling. Hence it appears that at 150° C. the gas is denser than water. Without knowing the exact composition of the enclosed gas and the variations from Boyle's Law that it would exhibit at high pressures and at a temperature of 150° C., it is not possible to ascertain to what extent it has been compressed. It is by no means unlikely that the carbonic acid now found in the liquid state in cavities was originally floating as a dense gas forming a sort of emulsion in the silica solution before its solidification took place.

IV. *On Crystal-shaped Cavities.*

In the course of my experiments I have frequently remarked the symmetrical arrangement of cavities around the axis of the crystals in which they were contained. Thus in a beryl, the cavities took the shape of tubes lying parallel to the six faces of the prism. In a hexagonal prism of quartz the cavities were of irregular shape, but so disposed round the principal axis that they were evidently caused by enclosures of water during successive growths of the crystal. Generally speaking, the cavities themselves are irregular in form and more or less rounded; especially is this the case in crystals artificially formed; but I have observed that in certain cases the cavities are not only angular, but that they take the form of the crystals in which they are enclosed so closely, that each side of each cavity is parallel with a face of the crystal. This has been seen in quartz porphyry from Arran; in granite from the Mourne Mountains; in Aberdeen granite; in the granite from Tudyvan, Cornwall; and in quartz from Snowdon. A glance at the illustrations will at once give an accurate idea of the appearance of the cavities as we see them; of course by transmitted light. The bubble will always be noticed near the centre or towards one end of the cavity. In the Arran porphyry the quartz takes the form of the double hexagonal pyramid, and so likewise do the cavities. The best and most striking, and at the same time most numerous examples of this symmetrical formation of cavities are to be met with in a prism of rock-crystal which I have had cut into sections, both parallel with and at right angles to the principal axis.

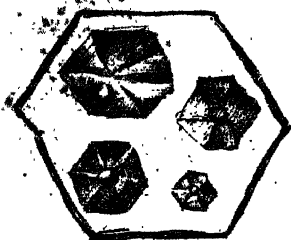
The cavities, as seen in both sections, are shown in Figs. *a* and *b*, and it will be noticed that there are a few of a prismatic shape, but the majority are simply double pyramids. Were it not for the presence of the bubbles, it would be impossible to believe that these

were not crystals of quartz enclosed. The following is what I conceive to be the origin of these symmetrical cavities. The mineral is crystallised at a high temperature, say 150°C. , for by raising the rock-crystal to this temperature I find the water entirely fills the cavities. The high temperature has diminished the tendency to cohesion. The water exerts a resistance to compression which is comparable with that of a solid body; but unlike that of a solid body the direction of the resistance can be changed, *i.e.*, the shape of the enclosed water can be altered so as to conform to the planes of crystallisation of the mineral; consequently we have the molecules of the silica grouped around the resisting liquid, as if they were arranged round another crystal as in the formation known as *capped quartz*. To show that these crystal-shaped cavities are not of rare occurrence, at least in some specimens, I have only to refer to Fig. c, which gives some idea of a complete chain of them, each one of which contains a fluid and a bubble. As the best and most regular crystals are formed slowly, so are these crystal-shaped cavities apparently formed more generally where the growth of the crystal has been gradual, that is to say where cavities are of rare occurrence, slowly grown crystals being to a great extent free from cavities.

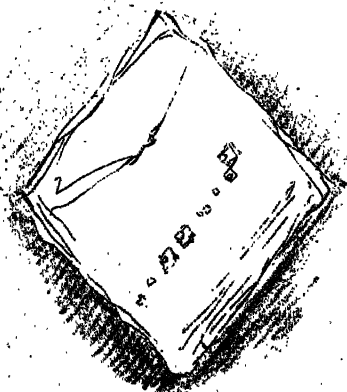
CRYSTAL-SHAPED CAVITIES.

Explanation of the Drawings.

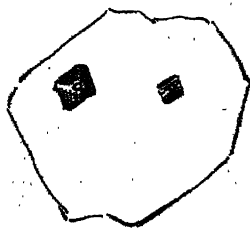
- a. Cavities in a transverse section of a crystal of quartz, evidently hollow six-sided pyramids. At the apex of each is seen a bubble, the liquid contents are water. The true outline of the section of the crystal is drawn in the position it was fixed in during observation. It will be noticed that the sides of the cavities are parallel to the faces of the crystal in which they are contained. $\times 250$ diameters. Sometimes as the cavities are obliquely inclined, they appear distorted, as for instance the one to the right in the drawing.
- b. Cavities seen in a longitudinal section of the same crystal. Many of these evidently resemble the double pyramid and other modifications of crystals. $\times 250$.
- c. A string of geometrical cavities observed in the same specimen. $\times 250$.
- d. Cavities taking the form of the quartz crystals in porphyry from Arran. The sides are parallel to the sides of the crystal. $\times 400$.
- e. Another crystal in the same specimen containing similar cavities. $\times 400$.



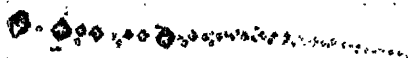
a.



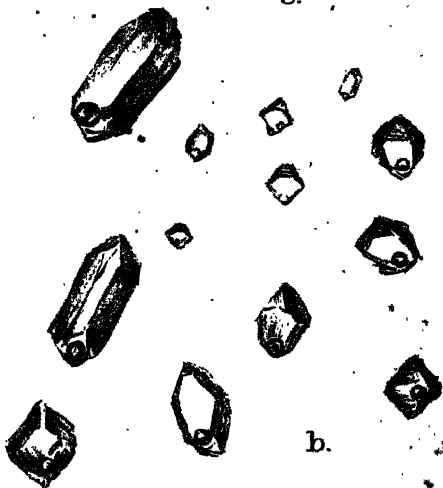
d.



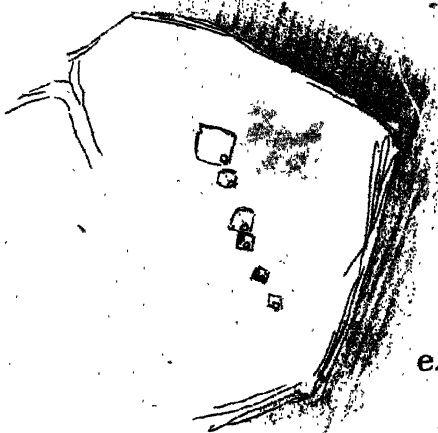
f.



c.



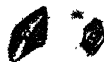
b.



e.



g.



h.

- f. Quartz with crystal-shaped cavity in granite from the Mourne Mountains. $\times 400$.
 g. The same in Aberdeen granite. $\times 400$.
 h. Crystal-shaped cavities in quartz from Snowden. $\times 400$.

VII. On Potassium Triiodide.

By GEORGE STILLINGFLEET JOHNSON, Daniell Scholar of King's College, London.

THE ready solubility of iodine in solution of potassium iodide has often been referred to as suggesting the existence of a polyiodide, but this was denied by Baudrimont (*Comptes rendus*, li, 827), who found that agitation with carbon disulphide removed the dissolved iodine from the liquid: on the other hand, it was shown by Jörgensen (*J. pr. Chem.*, ii, 347) that carbon disulphide failed to abstract the iodine from an *alcoholic* solution containing two atoms of iodine for each molecule of potassium iodide, whilst an *alcoholic* solution of potassium iodide completely decolorised a solution of iodine in carbon disulphide.

The probability of the existence of a triiodide of potassium was strengthened by Tilden's discovery of the triiodide of caesium, &c. (*Journ. Chem. Soc.* [2], iii, 99), to which Jörgensen added a number of similar compounds derived from other alkaloids (*J. pr. Chem.* [2], iii, 145—176, 328—348). I have succeeded in preparing the potassium triiodide in crystals by dissolving iodine to saturation in an aqueous or alcoholic saturated solution of potassium iodide and evaporating slowly over sulphuric acid. The crystals first deposited were dark-coloured cubes, which proved to be potassium iodide coloured by a little free iodine; but, after some days, lustrous dark blue prismatic crystals, sometimes two inches long, were deposited, which had the composition required by the formula KI_3 .

The first analyses were made by gently heating the crystals (dried over sulphuric acid) until potassium iodide alone remained.

Specimen 1. .789 grm. lost .49 grm.

„ 2. .717 „ „ .452 „

These numbers correspond with:—

	I.	II.	Mean.	Theory.
Potassium....	8.93	8.79	8.86	9.31
Iodine	91.07	91.21	91.14	90.69
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The excess of iodine, amounting to 0·448 per cent., appeared to be due to the extremely deliquescent character of the triiodide, which rendered it impossible to transfer it from the desiccator to the balance without increase of weight by absorption of moisture, and partly, perhaps, to the retention of water or mother-liquor in minute cavities in the substance of the crystals. In order to effect a more direct determination of the iodine, the triiodide was dissolved in water (containing some potassium iodide, to prevent precipitation of iodine), and the amount of the latter in excess of that required for the iodide, was determined by a standard solution of sodium hyposulphite, starch being used as an indicator.

Specimen 1. 1·623 grm. required 77·7 c.c. of a solution of sodium hyposulphite, of which 1 c.c. = ·01235 grm. of iodine.

Specimen 3.	(a.)	·6735 grm. required	32·5 c.c.
	(b.)	·2125 " "	10·1 "
	(c.)	·66 " "	31·5 "
Specimen 4.		·762 " "	36·2 "

These numbers correspond with :—

	I.	III.			IV.	Mean.	Theory.
		a.	b.	c.			
Potassium	9·63	9·51	9·73	9·67	9·73	9·65	9·31
Iodine ..	90·37	90·49	90·27	90·33	90·27	90·35	90·69
	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>

It will be observed that the iodine determined by the volumetric analysis is ·342 per cent. below that required by the formula KI_3 , since the apparent weight of the triiodide employed is increased by the inevitable absorption of moisture. The mean number obtained by the heating and volumetric methods of determination is 90·745 per cent. of iodine, which exceeds the theoretical number by only ·053 per cent.

Thinking it desirable to obtain a direct determination of the *potassium*, as well as of the iodine contained in this compound, the following method of analysis was employed.

A portion of dry triiodide was dissolved in an aqueous solution of sulphurous acid, and solution of nitrate of silver dropped in till no further precipitate subsided. Nitric acid having been introduced and the liquid boiled, the iodide of silver was collected and weighed. Excess of silver having been removed from the filtrate by hydrochloric acid, the resulting solution was evaporated to a small bulk; dilute sulphuric acid added; and evaporation carried to dryness. The residue was ignited with carbonate of ammonia, to convert bisulphate into neutral sulphate of potash, until a constant weight was obtained. The following results show the success of the above process :—

Specimen 1.	(a.)	2.097	grams gave	3.505	grams	AgI.
	(b.)	2.474	" "	0.504	"	K ₂ SO ₄ .
Specimen 2.	(a.)	1.744	" "	2.908	"	AgI.
	(b.)	1.8825	" "	0.394	"	K ₂ SO ₄ .

These numbers correspond with:—

	I.	II.	Mean.	Theory.
Iodine	90.310	90.11	90.21	90.69
Potassium ..	9.145	9.36	9.25	9.31
	99.455	99.47	99.46	100.00

The small deficiency in the percentage is due to the moisture absorbed by the salt. The mean of the two determinations gives the atomic ratio of K : I = 1 : 2.994.*

The potassium triiodide crystallises in long prisms which are almost black, and exhibit a lustre resembling that of iodine; it is extremely deliquescent, and can be preserved only in an atmosphere dried by sulphuric acid; when it is exposed to ordinary air, a film of moisture is immediately deposited, the gradually increasing thickness of which causes a rapid succession of colours resembling those formed in the tempering of steel. After a short time it becomes a brown liquid. If the crystals are exposed to air for even a few minutes, and then again allowed to dry over sulphuric acid, a film of potassic iodide, due to efflorescence of iodine, forms on their surface, destroying their metallic lustre, and, after two or three repetitions of such treatment, even producing a whitish crust of that salt, which, however, exerts a protective influence upon the triiodide beneath.

When the crystals of potassic triiodide are immersed in water, a portion of the iodine is deposited, the remainder being held in solution by the potassium iodide. It would appear probable that the triiodide is capable of existing only in concentrated aqueous solutions, since the saturated solution of iodine in potassium iodide always deposits the latter salt before any triiodide separates, and the latter, or its mother-liquor, when treated with excess of water, deposits iodine.

The triiodide is soluble in alcohol, in a very small quantity of water,

* It may be interesting to mention a slight obstacle which presented itself in the determination of potassium as sulphate of potash. In the first analysis, I found that prolonged and repeated ignitions were necessary in order to obtain a constant weight of sulphate, even when solution of carbonate of ammonia had been added to the contents of the crucible. The explanation of this difficulty was not at first obvious, but I at length found it to be due to the solubility of silver chloride in hydrochloric acid, leading to the retention of silver salt in the crucible, and necessitating prolonged application of heat to volatilize it completely.

or in a saturated solution of iodine in iodide of potassium, and is deposited in crystals on evaporation over sulphuric acid.*

The mother-liquor of potassic triiodide is a dark-coloured, heavy liquid, dark blue to reflected, and dark red to transmitted light. Its specific gravity is 3.13.

The determination of the *specific gravity* of the triiodide of potassium is attended with peculiar difficulties. Not only does the deliquescent nature of the crystals offer an obstacle to accuracy, but it is also necessary to make use of the mother-liquor, which is apt to deposit crystals sometimes for days after its removal from the drying chamber; and each deposit is followed by a change in the specific gravity of the remaining liquor. In the following experiments the crystals were introduced into the specific gravity tube in an atmosphere of dry carbonic acid gas, and the specific gravity of the mother-liquor was determined in each case immediately before its employment. The results are as follows:—

Experiment I.	3.494	
„ II.	3.503	
	2) 6.997	Mean 3.498.
	3.498	

The experiments were made at the temperature of the laboratory, viz., about 15° centigrade.

The *atomic volume* was determined by introducing the dry crystals into a volumometer flask, the neck of which was graduated in decigrams of water, and which had previously been filled up to the zero point with the mother-liquor of the salt.

1.188 gram of KI_3 made the liquid rise 3.4 divisions. The atomic volume of the triiodide would then be denoted by the number 120.2, and the specific gravity by the number 3.494.

The atomic weight of potassium triiodide being 420.1, and its specific gravity 3.498, its atomic volume would be $\frac{420.1}{3.498} = 120.1$.

The atomic volume of K = $\frac{39.1}{89.5} = 45.2$; and that of I = $\frac{127}{4.947} = 25.67$.

Now the sum of atomic volume of K = 45.2

and 3 × atomic volume of I = 77, is 122.2, whilst the

122.2

* Crystals of potassic triiodide may be obtained in a few days by mixing together iodine and potassic iodide in the proportion of 60.4 I to 39.6 KI, and dissolving in as little water as possible.

$$\text{sum of atomic volume of KI} = \frac{166.1}{3.056} = 54.3$$

$$\text{and } 2 \times \text{atomic volume of I} = 2 \times 25.67 = 51.34, \text{ is only } \frac{105.64}{105.64};$$

so that it appears that the triiodide of potassium does not consist of a molecule of potassium iodide, KI, united with a molecule of iodine, I₂, but of an atom of potassium, K, combined with 3 atoms of iodine, I, *without condensation*.

The low specific gravity of the triiodide is remarkable, when we consider the very high proportion of iodine which it contains, and interesting as a striking instance of the fact that the specific gravity of solid chemical compounds is high in proportion to the intensity of the chemical affinity which unites their components. (V. Braun.)

When gently heated, the triiodide fuses at about 45°, at which temperature but little iodine is evolved, and the fused mass solidifies in crystals when placed over sulphuric acid. At a higher temperature iodine is evolved and potassium iodide remains.

During the preparation of the crystals of triiodide, it was observed that the cubical crystals of potassium iodide, which were deposited at an early stage of the evaporation, were of the transparent variety, tinged brown by iodine, and intersected by dark lines diverging from the centre to the angles of the crystals; when the deposition of these crystals ceases, those of the triiodide begin to separate. During very warm weather, when the evaporation over sulphuric acid was very rapid, the crystals of triiodide had a tabular appearance, and were arranged in steps, like potassium iodide. In cooler weather, the dark liquid from which the potassium iodide had been deposited, sometimes remained over sulphuric acid for two or three days, without depositing any crystals, but on pouring it into another vessel, or agitating, an abundant crop of large crystals formed within two hours.

On one occasion some dendritic crystals formed in the mother-liquor of the triiodide, resembling those commonly formed in saturated solutions of ammonium chloride.

VIII.—*Researches on Colein.*

By A. H. CHURCH.

FOR several years past I have made experiments on a small scale with the hope of isolating the splendid colouring matter which renders the numerous varieties of *Coleus verschaffeltii* so attractive as ornamental-foliaged plants. This interesting Labiate contains, both in stem and leaf, a colouring matter having obviously many characteristics in

common with the singularly sensitive substance or substances to which violets, purple dahlias, iris, copper-beech, black grapes, and many other flowers, leaves, and fruits, ranging in colour from crimson to violet-blue, owe their varied hues. Although the investigation of colouring matters of this class is generally beset with difficulties, it appeared to me that a successful issue would be less unlikely to be reached in the case of the *Coleus* than of an ordinary plant. Commonly, an initial difficulty has arisen from paucity of material; the alterability of the colouring matter and its admixture with other colouring matters and with organic and mineral impurities have proved still more serious sources of vexation and delay. The first difficulty was removed effectually, thanks to Mr. Jackson, of Kingston, and to Dr. Hooker, Director of the Royal Gardens at Kew, from both of whom I received in the autumns of 1874 and 1875 an abundant supply of the stems of the desired plant. Indeed, I was obliged to decline several kind offers of further contributions of the raw material for my research, finding the rapid working-up of half-a-hundred weight of *Coleus* stems a task which taxed the resources of my laboratory to the utmost.

The method finally adopted in order to isolate the colouring matter to which I now wish to direct the attention of the Society, may be briefly outlined as follows:—The leaves of the selected plants are rejected, along with such paler portions of the stems as are greenish or deficient in pigment. The chosen parts are introduced without delay into an apparatus in which they can be reduced to a pulp. I found a porcelain sausage-machine far better than the large wedgwood mortar which I first employed for this purpose. During the crushing process, a slender stream of strong alcohol, faintly acidulated with sulphuric acid, falls upon the bruised mass. The crimson pulp thereby prepared is submitted to strong pressure (avoiding contact with metal), the deep crimson liquor from it being strained first through cambric and then through Swedish paper; the squeezed pulp is then again exhausted with strong alcohol. The united liquors may now be shaken with a little moist precipitated barium carbonate, and afterwards again filtered. They are then introduced into a capacious retort immersed in a water-bath, most of the alcohol being thus removed by distillation. If this process be carried far enough, a mass of deep-coloured, resinous-looking substance sinks to the bottom of the retort, while a rich-red liquid remains above it. The resin is the colouring matter, but not pure; the liquid also contains the same substance, part of which may be separated from it by further evaporation at a gentle heat. But the remaining liquor retains much colouring matter in solution, owing to the solvent action of the organic acids, sugar, and other substances which are likewise present. By dilution with much

water and subsequent repose, a further separation of more colouring matter may be caused.

So far we have described the extraction of the colouring matter in the form of a resinous mass, plastic when warm, and almost liquid when originally deposited. I did not at once ascertain the best and most thorough way of purifying this product, but was content to agitate its alcoholic solution with barium carbonate, and then to precipitate the colouring matter from the filtered liquid by pouring it into absolute ether. It will be convenient here to assign the provisional name of *colein* to the product now being described, not because I wish it to be regarded as new, but in order to avoid an awkward periphrasis, and the assumption that it is identical with similar colouring matters which have been previously named.

An early analysis of colein may be cited here, not because it afforded numbers which were subsequently confirmed, but in order to afford some notion of the tedious steps by which the inquiry progressed; for it was necessary to test every modification of the processes of purification and preparation by means of quantitative analysis.

Analysis I. Colein, prepared from red resin by repeated solution in alcohol, filtration, evaporation, and washing of residue with ether. This specimen was dried *in vacuo* over sulphuric acid.

·4224 gram gave ·7893 gram CO_2 and ·196 gram H_2O .

·3914 " ·0034 " ash = ·86 per cent.

·405 " ·0345 " PtAm_2Cl_6 by combustion with soda-lime = ·54 per cent. N.

1·2395 gram lost ·0247 in water-oven = 2·0 per cent.

Thus the obvious impurities amounted to 3·4 per cent., but in reality the nitrogen and the ash represented much larger quantities of intruding substances; for the ash was derived from the lime and potash salts of both organic and inorganic acids; while the nitrogen occurred mainly as a compound of an alkaloid closely resembling nicotine. It is, therefore, impossible to effect an adequate correction in the analytical numbers by means of a mere deduction of ash, moisture, and nitrogen from the substance taken, and of water from the total water weighed in the calcium chloride tube. But the resulting percentages are interesting, so far as they go, in connection with the later results. They are—

Carbon, 52·73 per cent. Hydrogen, 5·11 per cent.

Analysis II.—The next specimen analysed had been prepared by repeated solution in alcohol and a final precipitation by means of absolute ether. It was nearly free from nitrogen and ash, but was not quite dry, having been merely kept over sulphuric acid *in vacuo* till

constant in weight. Burnt with copper oxide, in a platinum boat, in a current of oxygen, it gave these results*—

·288 gave ·594 CO₂, ·1396 H₂O, ·0015 ash.

Deducting ash, these numbers corresponding with the following percentages:—

Carbon, 56·54. Hydrogen, 5·41. Oxygen, 38·05.

A trace of alcohol was found to have been retained by this preparation, and thus the percentage of hydrogen was raised and that of carbon lowered.

Analysis III.—The sample employed for this analysis had been prepared from the lead-compound of colein, to which I have to refer again shortly. By decomposing this lead salt with sulphuric acid in strong alcohol, and then evaporating the alcoholic filtrate, and further purifying the colein present by the means already described, a nearly pure product was obtained. It was dried *in vacuo* first, and then at about 90° C. The results were: ·4968 gave 1·0329 CO₂. ·2144 H₂O. ·0013 ash. Deducting ash, these results correspond with the following percentages:—

Carbon, 56·85. Hydrogen, 4·80. Oxygen, 38·35.

Analyses IV, V, and VI. Colein purified by treatment with alcohol and ether as before, then dissolved once more in alcohol and precipitated by *water*. This process proved to be an excellent one, and was adopted in all subsequent operations. The three analyses here given were made with the same sample dried at about 90°. It was, however, found that traces of alcohol obstinately adhered to it.

	Colein taken.	CO ₂ .	H ₂ O.	Ash.
IV	·4602	·949	lost	·0035
V	·4125	·846	·1943	·0037
VI	·446	·9135	·2087	·0035

The corresponding percentages are:—

	IV.	V.	VI.
Carbon	56·67	56·41	56·30
Hydrogen	—	5·26	5·24
Oxygen	—	38·33	38·46

Analyses VII to XI. The colein for these analyses had been prepared and purified in the same manner as that last described; it was dried in the water-oven. The hydrogen of all the analyses showed an

* The weights referred to here and throughout the paper are grams and decimals of a gram; the same method of combustion was employed in all the analyses.

extreme range of no more than .16 per cent., but the fluctuations in the carbon were too large to be satisfactory. It was found that a slight error, arising from imperfect removal of CO_2 from the oxygen used, had vitiated the results of Analyses VII to IX, so far as the carbon is concerned. Analyses X and XI were made after the chance of such experimental error recurring had been prevented.

	Colein taken.	CO_2 .	H_2O .	Ash.
VII....	.4427	.9542	.2005	.001
VIII ..	.4285	.9257	.1935	.002
IX4415	.9499	.194	.0015
X4375	.9275	.1988	.001
XI4687	.9915	.2095	.0015

The corresponding percentages, after deduction of the ash, are—

	VII.	VIII.	IX.	X.	XI.
Carbon	58.91	59.19	58.88	57.95	57.69
Hydrogen ..	5.04	5.04	4.90	5.06	4.96
Oxygen	36.05	35.77	36.22	36.99	37.45

Analyses XII and XIII. Colein purified by alcohol, ether, and precipitation and much washing with water at 50° — 60° C.; dried in air-bath at 100° . This sample was practically pure.

	Colein taken.	CO_2 .	H_2O .	Ash.
XII447	.9429	.202	.001
XIII524	1.098	.24	.002

The corresponding percentages are—

	XI.	XII.
Carbon	57.66	57.37
Hydrogen ..	5.02	5.10
Oxygen	37.32	37.53

Amongst the preceding thirteen analyses, there are five which I believe represent accurately, from one cause or another, the composition of pure colein. In other cases some defect in the mode of preparation or desiccation of the sample, or else in the combustion-process itself, has interfered with the accuracy of the results. I am, however, of opinion that the singular difficulty of dealing with substances of the class to which colein belongs, justifies and explains the range in the percentages deduced from the majority of the analyses cited: this range in fact is not a very wide one. The percentages from the five analyses, which, critically examined appear to me to be most deserving of acceptance, are here arranged—

No. of analysis.	Preparation.	Per cent. carbon.	Per cent. hydrogen.
III ..	From lead-salt	56.85	4.80
X.	{ Purified by alcohol, ether, } and water.	57.95	5.06
XI ..		57.69	4.96
XII. .	{ Treated similarly to last, but } with water at 50°—60°.	57.66	5.02
XIII. {		57.37	5.10

The mean percentages deduced from the above analyses are given below; and, for comparison, the percentages required by the formula $C_{10}H_{10}O_5$ —

	Experiment.	Theory.
Carbon	57.50	57.67
Hydrogen ..	4.99	4.76
Oxygen	37.51	37.57

We will now see how far the suggested formula is confirmed by the analysis of the lead-salt.

Colein lead-salt—The most satisfactory compound of colein which I have yet been able to obtain was this lead-salt; its preparation was conducted thus:—Ordinary neutral lead acetate was dissolved in alcohol of 70 per cent., the solution was filtered. Pure colein in powder was then dissolved in another portion of the same alcohol; the two solutions were then mixed, decided excess of lead acetate being used. The dull indigo precipitate was washed with weak alcohol and then with water free from carbonic acid, until all soluble lead-salts were removed; it was then dried *in vacuo* over sulphuric acid. Such part of the dried mass as had been in contact with the porcelain surface of the basin showed a faint coppery lustre.

Analysis XIV. Colein lead-salt, dried in water-oven. .638 gave .924 CO_2 , .1803 H_2O .

Analysis XV. Colein lead-salt, another preparation, dried at 100°. .4518 gave .6626 CO_2 , .131 H_2O .

Analysis XVI. Colein lead-salt, another and purer preparation, dried at 100°. .453 gave .6299 CO_2 , .121 H_2O .

Analysis XVII. Colein lead-salt, same as last, dried at 100°. .491 gave .2365 $PbSO_4$.

Translated into percentages, these results become—

	XIV.	XV.	XVI.	XVII.
Carbon	39.49	39.99	37.92	—
Hydrogen ..	3.14	3.23	2.96	—
Lead	—	—	—	32.9
Oxygen	—	—	—	—

The preparation represented by analyses XVI and XVII was subsequently ascertained to be purer than the earlier specimen analysed,

which contained some free colein. We must therefore employ the percentages derived from the two last analyses in comparing experiment and theory.

	Experiment.	Theory, $C_{20}H_{18}PbO_{10}$.
Carbon	37.92	38.40
Hydrogen	2.96	2.88
Lead	32.90	33.12
Oxygen	26.22	25.60

I think that the empirical formulæ which I have suggested for colein and its lead-salt are rendered extremely probable by the results of the analysis of those preparations in the purity of which I feel the greatest confidence. Further endeavours to estimate the molecular weight of colein by means of watching the changes of colour wrought in its solution by means of standard acids and alkalis have not done much in elucidating this question. I hope that some new metallic derivatives of colein and some compounds with organic bodies, which I expect to be able to prepare, may decide this point.

It remains now to give a description of the physical and chemical properties of colein, to compare it with kindred compounds, and to note its mode of occurrence in the particular plant from which my supplies have been derived.

Colein when pure is a brittle solid of resinous aspect and conchoidal fracture. The colour of its powder is reddish-purple, but it usually shows a colour verging upon crimson, owing to the presence of a trace of acid. It dissolves freely in moderately strong alcohol with a colour, which is perhaps best described as somewhere between crimson and violet; in absolute alcohol (distilled fresh from sodium), even when warm, it is, when itself dry, much less soluble. The alcoholic solution of colein, if neutral, soon loses its colour, owing, as I conclude, to no reduction of the colein, but merely to its union with a portion of the alcohol. The full intensity of the original colour may be restored by the removal of the alcohol in a current of hydrogen, while a drop of sulphuric acid gives an equally marked red reaction with an alcoholic solution which has been kept till nearly colourless, and with one that has but just been made. It is beautiful to watch a nearly colourless solution of colein recover its hue as it is being warmed, to drive off the alcohol, on the steam-bath. The disappearance or fading of the colour of colein solutions, both alcoholic and aqueous, is prevented by the presence of acids, and, in some degree, of certain salts and organic compounds. Colein is but slightly soluble in water, and quite insoluble in ether, both of these liquids precipitating it from its alcoholic solution—the latter completely, the former imperfectly and somewhat slowly. If the colein,

after precipitation by water, be gently warmed under water, it will partially fuse at 50° — 60° C., and in that condition scattered particles may be welded into a single mass or drawn out into threads. When dry it is not fusible at 100° . At higher temperatures it gives off traces of a thymol-like substance and leaves a bulky charcoal.

By acids a solution of colein is reddened, the quantity of acid necessary to produce this effect being very small, so small indeed, as to make it probable that colein is really a red acid itself, but that its colour is generally modified by a trace of ammonia in the acid solution; and the test-papers imbued with it keep their colour well. On the gradual addition of a weak solution of ammonia to a colein solution, a series of changes in its colour occur, the order being purple, violet, indigo, chrome-green, and greyish-yellow. When once the yellow stage has been reached, the colein has been profoundly altered and is no longer susceptible of being reddened by an acid. On examining the absorption spectra of these acid, neutral, and alkaline solutions, it will be found that their shaded portions do not present very definite features. However, it may be stated that it is possible to reproduce the exact spectrum of the coloured contents of a cell of the coleus stem by means of a neutral solution of colein, thus negating the idea that colein might be a product rather than an educt. It may be stated that the red acid solution of coleus shows a slight shade over the farther red of the spectrum up to about 31 on a scale where the E line is 71, the D line 50, and the C line 34. The space between 32 and 58 or 59 is bright, but a very decided absorption begins at 59, and cuts off the green and a little of the blue of the spectrum. The solution assumed to be neutral shows a narrower unobscured space lying between 32 and 51; the band at 51 is very decided up to 58 and shades off beyond. The green alkaline solution of colein has the red more obscured, especially about 32; the bright space between this and the second dark band is very narrow, the latter band beginning at about 41 and attaining its greatest blackness about 46: this band soon becomes very faint, and almost disappears at 59 in weak solutions.

I do not give these measurements as having any claim to exactness; but they may serve as helps in identifying colein with some of those colouring matters which have received different names, but which are certainly not far removed from it. Spectroscopic examination of such substances should, however, always be connected with the completest chemical investigation, including ultimate analysis, or differences will be found where none exist. The acid, neutral, or alkaline reaction of the solution, the presence of other compounds not themselves coloured, and the marked influence of different solvents will, in many cases, render spectroscopic results, unless supported by chemical analysis, most misleading.

With concentrated sulphuric acid colein forms an orange-coloured liquid which, on dilution with water, presents the red colour and other characters of an acid solution of unaltered colein. It is dissolved with a crimson colour by acid of sp. gr. 1.53. In either case, if only enough acid to dissolve it be used, much of the colein may be reprecipitated on the addition of water. Nitric acid converts colein into a brown resinous mass. Caustic alkalis—even ammonia—profoundly alter colein, but no definite products have yet been found. Of all the reactions which colein furnishes with metallic salts not yet named in this paper, that with stannic chloride is the most interesting. A splendid violet precipitate, apparently permanent, is produced when this chloride is added to a strong alcoholic solution of colein. This tin compound awaits investigation.

The distribution of the colouring matter in the plant demands a word or two of explanation. In the leaves it is confined mainly to the epidermal cells and to the hairs connected therewith. In the stem it occurs quite capriciously distributed, not only in the epidermis and hairs, but also in abundance in many parts of the parenchyma of the pith. Occasionally it may be seen in a few parenchymatous cells bordering the fibro-vascular bundles, but it is absent from the vessels themselves and from the whole cortical tissue. Its mode of occurrence in the hairs of the stem and leaf of the plant is most curious. A hair having, say six cells, may have the terminal cells richly tinted and all the others free from colein. It has clearly been formed throughout the plant *in situ*. It is also a substance of lower physiological position than the less oxidised chlorophyll.

A careful comparison of colein with such colouring matters as those named cyanin, erythrophyll, oenolin, &c., has yet to be made. I am quite aware of the importance of such comparison, but I cannot promise to undertake so laborious a study until I have further elucidated the real nature of colein itself. It must be confessed that all the chemical evidence yet obtained points to the identity of colein with the *anthocyan* of Marquart, the *cyanin* of Frémy and Cloëz, the *erythrophyll* of Morren, and with the *oenolin* extracted from red wines by Glénard. I confess to my ignorance of the results obtained by this last chemist until my own analyses had been completed. He obtained a colouring matter which agreed not only in all its recorded characteristics with colein, and indeed with the substances described under the three names just cited, but in centesimal composition also. Glénard analysed the substance itself and its lead-salt, and was thus led to adopt the same formulæ as those which my analyses support. Should all these colouring matters prove identical, as I strongly suspect, Glénard's name of oenolin may perhaps deserve

the preference, should his formula be confirmed. Anthocyan may claim priority of description, but not of analysis.

To my assistant, Mr. R. C. Woodcock, my best thanks are due for the care which he has bestowed upon the analytical work involved in this research.

IX.—On some Derivatives of Dithymyltrichlorethane.

By Dr. EMIL JÄGER.

I HAVE elsewhere (*Ber. d. Deutsch. Chem. Ges.*, vii, 1197) shown that a white resinous precipitate is produced when sulphuric acid diluted with one-third of its volume of glacial acetic acid is added to a mixture of one molecule of chloral and two molecules of thymol, care being taken that the temperature of the mixture shall always be kept low.

A solution of this precipitate in alcohol deposits on evaporation white crystals of dithymyltrichlorethane, belonging to the monoclinic system, and melting at 194°. The composition of this body is

$\text{CCl}_3 \cdot \text{CH} \begin{matrix} \diagup \text{C}_{10}\text{H}_{12}\text{OH} \\ \diagdown \text{C}_{10}\text{H}_{12}\text{OH} \end{matrix} + \text{C}_2\text{H}_6\text{O}$, and the above reaction is represented as follows:—



That dithymyltrichlorethane contains the hydroxyls of thymol is shown by the fact that it forms diacetyl- and dibenzoyl-compounds.

By acting with strong oxidising agents upon dithymyltrichlorethane, as well as upon most of its derivatives, yellow crystals are obtained which can be volatilized in a current of steam, and prove to consist of almost pure thymoquinone. Hence it would appear that the aldehyde residue is linked to that carbon-atom of thymol which is attacked on oxidising the latter to form the quinone.

When heated with zinc-dust, dithymyltrichlorethane exchanges its chlorine for hydrogen, and produces, not only the saturated dithymylethane, but likewise the non-saturated dithymylethene.

Dithymylethane, $\text{CH}_3\text{CH} \begin{matrix} \diagup \text{C}_{10}\text{H}_{12}\text{OH} \\ \diagdown \text{C}_{10}\text{H}_{12}\text{OH} \end{matrix}$ crystallises in large, white rounded plates, melting at 180°. It dissolves in most of the usual solvents with the exception of water. Weak reagents do not affect it, but stronger ones destroy the molecule completely.

Dithymylethene, $\text{CH}_2=\text{C} \begin{matrix} \text{C}_{10}\text{H}_{12}\text{OH} \\ \text{C}_{10}\text{H}_{12}\text{OH} \end{matrix}$, forms needle-shaped crystals

which melt at $170-171^\circ$. It is rather more soluble than the foregoing compound, but is also quite insoluble in water.

Weak oxidising agents exert a most remarkable action upon this body. When a dilute alcoholic solution is treated with potassium ferrocyanide, small green crystals are formed. If, before the addition of the ferrocyanide, the solution is rendered alkaline by the addition of a small quantity of carbonate of soda or of ammonia, the green colour of the crystals is no longer seen, but a flocculent red precipitate falls down, and this when dissolved in chloroform is again deposited in the form of dark-red crystals.

Analysis of the *green* crystals gave the following results:—

0.1850 gram yielded 0.5542 gram CO_2 and 0.1394 gram H_2O .

This agrees closely with the formula $\text{C}_{44}\text{H}_{54}\text{O}_4$.

	Calculated.	Found.
C.	81.73	81.69
H	8.35	8.37

The melting point is $214-215^\circ$. They resist the action of nearly all solvents, with the exception of toluene and chloroform, from which they may be recrystallised, although considerable loss is experienced in the process.

Analysis of the *red* crystals gave the following results:—

0.1542 gram gave 0.4633 gram CO_2 and 0.1134 gram H_2O , corresponding to the formula $\text{C}_{22}\text{H}_{26}\text{O}_2$.

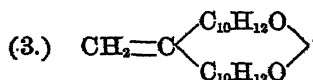
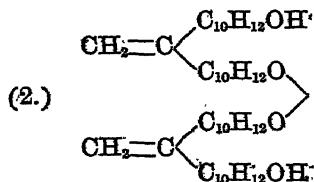
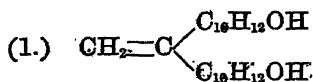
	Calculated.	Found.
C.	81.99	81.93
H	8.07	8.17

When heated to 215° the red crystals melt, forming a brown liquid.

They dissolve easily in chloroform, but are nearly insoluble in all other solvents, whilst acids and alkalis, even in a very weak state, decompose them readily.

A mixture of dithymylethene and the red crystals dissolved in chloroform deposits on evaporation the above-described green needles.

The same relation which exists between hydroquinone, quinhydrone, and quinone, appears to hold good between *dithymylethene* and these two products of its oxidation. Hence it would appear not inappropriate to call the green crystals *dithymylquinhydrone*, and the red ones *dithymylquinonethene*, thus:



The quinone can be easily reduced to dithymylethene by sulphurous acid in the cold, if suspended in the original flocculent state in alcohol, but when once crystallised, it requires boiling in order to dissolve it. At a temperature of 100° , however, the sulphuric acid formed by the reaction proves sufficient partially to decompose the substance, and only a small quantity of dithymylethene is formed, together with a large quantity of a resinous matter. A better method, however, is to reduce the quinone with zinc-dust and acetic acid, as in this way the formation of resinous matter is avoided.

By means of this reaction pure dithymylethene can easily be produced. It is only necessary to treat the impure mixture of dithymylethene and dithymylethane obtained by the action of zinc-dust on dithymyltrichlorethane, with weak oxidising agents, which act only on the ethene-compound, and convert it into the insoluble quinhydrone, which is then again reduced as described above.

THE OWENS COLLEGE, MANCHESTER,

June, 1876.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Theory of Luminous Flames. By KARL HEUMANN (*Liebigs Annalen*, clxxxiii, 102—140).—This paper, the third of a series on the same subject, contains the results of the author's experiments on the effect of cooling and heating luminous flames. The results are summed up as follows:—

A cold object, such as a metal wire, brought into contact with a luminous flame, not only extinguishes that portion of the flame immediately surrounding it, but also destroys the luminosity of a much larger part of the flame.

As a rule, carbonaceous illuminating materials may burn with or without separation of carbon (*i.e.*, with luminous or non-luminous flames), according as the temperature of the flame is sufficiently high or not. Combustibles diluted with indifferent gases require a higher temperature to cause separation of carbon than when not so diluted.

The deposition of soot on objects brought into a luminous flame is not a consequence of cooling; on the contrary, reducing the temperature of a flame prevents, either partially or entirely, the separation of carbon. Soot is deposited even on red-hot surfaces, but it burns away rapidly in contact with air.

Gas-burners of iron or other good conductors of heat prevent the luminosity of the lower part of the flame to a greater extent than burners of steatite. When a gas-burner is heated to redness, the amount of light produced by the combustion of the gas issuing from it is considerably increased, the consumption remaining the same; and this increase is greater the smaller the consumption of gas.

The effect of heating the burner is two-fold. The luminosity is intensified, and at the same time it extends lower down the flame. Carbon is separated sooner, and more strongly heated. J. R.

The Specific Rotatory Power of Glucose (Grape-sugar). By B. TOLLENS (*Deut. Chem. Ges. Ber.*, ix, 1531—1538).—In his previous researches with solutions containing from 3—10 grams in 100 c.c., the author found that the mean rotation for the hydrate $C_6H_{12}O_6 + H_2O$ was about 48.47° , and for the anhydride about 53.10° . Further experiments show that in concentrated solutions the specific rotation of glucose rises with the degree of concentration up to 53.36° for the hydrate and 58.70° for the anhydride, and these results agree with the observations of Landolt (*Berichte*, ix, 901). The rotatory power of the solution may be calculated by the formula—

$$(a) D = 47.92541 + 0.015534 P + 0.0003883 P^2.$$

where $(\alpha)_D$ is the specific rotation for sodium light, and P is the percentage weight of the solution. The anhydride must previously be multiplied by 1.1 to convert it into the hydrate. If we take instead of the percentage of the rotatory substance that of the solvent (q), as Landolt does, the formula becomes—

$$(\alpha)_D = 53.36181 - 0.093194 q + 0.0003883 q^2.$$

G. T. A.

Sensitiveness of Silver Bromide to the Green Rays as modified by the presence of other Substances. By M. CABRY LEB (Am. J. of Sci. [3], xi, 459—461).—The object of the researches described in this paper was to determine whether the sensitiveness of silver bromide for green rays is really enhanced by the addition of red colouring matters to the photographic film. Not one of the number of red pigments tried by the author produced the alleged effect, with the single exception of corallin; and in this case the increase of sensitiveness was much more marked with the red rays than with the green. Nor does the heightened effect depend on the colour of the corallin; for the presence of a weak acid, in quantity insufficient to change the colour, completely destroys the power of the corallin to exalt the sensitiveness for the green rays. On the other hand many colourless substances were found, of which some increased and others decreased the sensitiveness to green light. The author points out that photographic effects depend upon several distinct factors, namely, the sensitiveness of the film, the time of exposure, the intensity of the light, and the development. Variations in any one of these particulars will give rise to very different results, even in cases where the remaining conditions are identical; and this circumstance introduces much risk of erroneous conclusions being drawn.

R. R.

Polarisation of Electrodes in Water free from Air. By J. A. FLEMING (Phil Mag. [5], 1, 142—148).—"When an electrolyte (dilute sulphuric acid) flows in a very strong magnetic field, the electromotive force generated by its motion effects the electrolysis of the liquid, such electrolysis being held to be proved by the subsequent polarisation of the electrodes." This statement of the author was objected to on the ground that the polarisation observed was due to the presence of dissolved air. This objection is met by the experiments here detailed.

A tube 30 c.m. long and $2\frac{1}{4}$ c.m. wide was closed at one end by an india-rubber stopper, through which passed two platinum wires carrying chemically clean platinum plates. The tube was filled with well boiled dilute sulphuric acid, the air pumped out by a Sprengel pump, and the vacuum maintained for several days. An arrangement capable of producing a very small electromotive force was employed, and a very sensitive mirror galvanometer included in the circuit. The experiments were then performed as follows:—

- (1.) The electrodes were made perfectly neutral.
- (2.) The galvanometer was excluded from the circuit, and a direct current sent through the decomposing cell for one minute.
- (3.) The polarisation was measured by the swing made by the gal-

vanometer needle when the electrodes were suddenly connected with it.

(4.) The swing made by the needle when the same current was started through the cell and galvanometer in one current was observed, the platinum plates having been brought to a neutral position.

Experiments were first made with water freed from air, and secondly with thoroughly aerated water. In both cases the same results were obtained (tables are given), but it was observed that whereas in the aerated liquid the polarisation rapidly disappears, in the air-free liquid it is very troublesome to get rid of the last traces.

In order to show that electrolysis really takes place, a tube containing platinum plates was so arranged that a current of acidulated water could be made to pass through it. The tube being full of acid, the plates were polarised feebly, and it was found that if the current was made to pass slowly, the polarisation of water was scarcely diminished, but if it flowed violently, so as to wipe off the adhering gases, the polarisation was entirely destroyed.

This experiment seems to point out that polarisation is in all cases only unseen electrolysis.

F. D. B.

Molecular Volumes of Sulphates and Selenates. By OTTO PETERSSON (*Deut. Chem. Ges. Ber.*, ix, 1559—1566).—A. *Constitution of Double Salts*.—The sulphates and selenates of K, Am, Rb, Cs, have the following volumes:—

Diff. from K-Salt.	Sulphates. K_2SO_4 .	Diff. of Volume.	Selenates. K_2SeO_4 .	Diff. from K-Salt.
0	65.37	6.54	71.91	0
	Am_2SO_4 .		Am_2SeO_4 .	
9.19	74.56	6.89	81.45	9.54
	Rb_2SO_4 .		Rb_2SeO_4 .	
7.90	73.27	6.70	79.97	8.06
	Cs_2SO_4 .		Cs_2SeO_4 .	
22.8	88.1	6.5	94.6	22.7

This table shows—

(1.) That in the series of sulphates and selenates of K, Am, Rb, Cs, the molecular volume is regularly increased by 6.6 when the group SO_4 is exchanged for the group SeO_4 .

(2.) That the substitution of Am_2 , Rb_2 , Cs_2 for K_2 produces an increase of volume of 9, 8, 23 in the selenates as in the sulphates.

The same regularity of increased volume shows itself in the double salts.

(α.) *Alums.*

Diff. from K-Salt.	Sulphates.	Diff. of Volume.	Selenates.	Diff. from K-Salt.
0	$K_2Al_2(SO_4)_3 + 24H_2O$ 541·6	$26·4 = 4 \times 6·6$	$K_2Al_2(SeO_4)_3 + 24H_2O$ 568·0	0
10·6	$Am_2Al_2(SO_4)_3 + 24H_2O$ 552·2	$26·4 = 4 \times 6·6$	$Am_2Al_2(SeO_4)_3 + 24H_2O$ 578·6	10·6
9·4	$Rb_2Al_2(SO_4)_3 + 24H_2O$ 551·0	$25·2 = 4 \times 6·3$	$Rb_2Al_2(SeO_4)_3 + 24H_2O$ 576·2	8·2
27·6	$Cs_2Al_2(SO_4)_3 + 24H_2O$ 569·2	$26·4 = 4 \times 6·6$	$Cs_2Al_2(SeO_4)_3 + 24H_2O$ 595·6	27·6

In the chrome-alums the difference of volume shows itself clearly between the sulphates and selenates; the difference between K_3 , Rb_3 , Am_3 is not so clear.

Sulphates.	Diff. of volume.	Selenates.
$K_3Cr_2(SO_4)_3 + 24H_2O$ 542·2	$28·8 = 4 \times 7·1$	$K_3Cr_2(SeO_4)_3 + 24H_2O$ 571·0
$Am_3Cr_2(SO_4)_3 + 24H_2O$ 553·6	$23·8 = 4 \times 6·0$	$Am_3Cr_2(SeO_4)_3 + 24H_2O$ 577·4
$Rb_3Cr_2(SO_4)_3 + 24H_2O$ 554·6	$22·2 = 4 \times 5·5$	$Rb_3Cr_2(SeO_4)_3 + 24H_2O$ 576·8
$Tl_3Cr_2(SO_4)_3 + 24H_2O$ 554·2	$22·4 = 4 \times 5·6$	$Tl_3Cr_2(SeO_4)_3 + 24H_2O$ 576·6

The volumes of the iron-alums are as follows:—

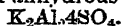
$$\left. \begin{array}{l} K_3Fe_2(SO_4)_3 + 24H_2O = 551·4 \\ Am_3Fe_2(SO_4)_3 + 24H_2O = 559·4 \\ Tl_3Fe_2(SO_4)_3 + 24H_2O = 568·2 \end{array} \right\} \text{difference} = 8·0$$

Alums could not be obtained from iron and selenic acid.

Sodium-aluminium selenate has a smaller volume than the sulphate, a relation without example in the whole series of sulphates and selenates; while thallium-aluminium selenate is anomalous in the opposite direction. Perhaps the molecules of the water of crystallisation are not in the same state of condensation in these two as in the other alums.

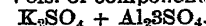
It is worthy of note that the molecular volumes of the alums investigated lie between 541 and 596. The volumes of the sulphate-alums lie between 541 and 569, those of the selenate-alums between 568 and 596, so that the last member of the sulphate series ($Cs-Al$ alum) and the first of the selenate series have the same volume. It would thus seem that the K , Am , Rb , Cs -salt is contained unaltered in the alums. To determine this point an attempt was made to separate the water from the alum, but this was successful only in the case of potassium-aluminium sulphate (by careful heating for a week).

Vol. of anhydrous alum.



192.46

Vols. of components.



65.86 126.42 = 191.78

Hence when an alum can be obtained in the anhydrous state its volume exactly equals the sum of the volumes of its components.

β. *Double Sulphates and Selenates of Co, Ni, Cu.*—These salts confirm the hypothesis that in double salts the components are contained unaltered. This is more obvious in the case of the selenates, and a table is given to show that the volumes of the double salts are equal to the sums of the volumes of their components. A second table shows that the usual difference of volume (6.0 or a multiple of 6.0) exists between the selenates and sulphates of Cu, Ni, Co, with K and Am, and also the difference between the Am and K salts. Favre and Valson concluded from their experiments that the double salts cannot exist in aqueous solution, but are formed at the moment of crystallisation. The author shows that as no contraction takes place on crystallisation, these salts may be supposed to exist in the same state in solution as after crystallisation, though the double salt of thallium is an exception.

B. Volumes of the Sulphates and Selenates of the rare Metals.

Sulphates.	Diff. of volume.	Selenates.
$Y_2SO_4 + 8H_2O$		$Y_2SeO_4 + 8H_2O$
240.4	$17.8 = 3 \times 6.0$	258.2
$Er_2SO_4 + 8H_2O$		$Er_2SeO_4 + 8H_2O$
238.6	$21.4 = 3 \times 7.1$	260.0
$Th_4SO_4 + 18H_2O$		$Th_4SeO_4 + 18H_2O$
425.0	$25.6 = 4 \times 6.4$	450.6

The following table also shows the difference between the volumes of anhydrous and crystallised sulphates:—

Anhydrous.	Diff. of volume.	Crystallised.
Y_2SO_4		$Y_2(SO_4)_3 + 8H_2O$
178.5	$61.9 = \text{vol. of } 8H_2O$	240.4
Er_2SO_4		$Er_2(SO_4)_3 + 8H_2O$
178.6	$60.0 = \text{,, } 8H_2O$	238.6
Di_2SO_4		$Di_2(SO_4)_3 + 8H_2O$
155.6	$96.4 = \text{,, } 8H_2O$	251.0
La_2SO_4		$La_2(SO_4)_3 + 9H_2O$
157.0	$97.8 = \text{,, } 9H_2O$	254.8

G. T. A.

An Improvement of Hofmann's Vapour-density Apparatus. By C. ENGLER (*Deut. Chem. Ges. Ber.*, ix, 1419—1421).—In using naphthalene-vapour for the determination of vapour-densities, several difficulties are encountered; the tubes easily get stopped up by solid

naphthalene, and the mercury is too suddenly heated, and cracks the barometer-tube, &c. To avoid this, the lower part of the outer tube is surrounded by a kind of Liebig's condenser, which is filled with paraffin-oil, and can be heated by an arrangement like that of a hot water funnel. C. S.

Employment of Compressed Air in Filtering Solutions. By W. LEÜBE (*Dinyl. polyt. J.*, ccxxi, 347).—Two funnels of copper-sheet are made to fit one upon the other at the open ends, so as to be air-tight, and are secured for this purpose by screw-threads. The one is thus screwed down upon the other. In the lower funnel is a glass one inserted, which fits accurately, and is made quite secure by cement. The small end of the lower funnel passes through an india-rubber stopper, through which also a bent tube passes. The india-rubber stopper fits air-tight into a glass bottle, in which the filtrate collects. In the glass funnel is placed a small platinum-foil funnel, and into this the paper filter fits. The tube of the upper funnel is connected by an india-rubber tube with the tap of the apparatus which delivers the compressed air. When the compression and suction are combined, a considerably accelerated rate of filtration is the result, over that obtained with either method singly.

The following table gives information as to the advantage obtained:—

Drops of filtered Fluid per minute.

Under ordinary atmospheric pressure.	With compressed air.	By suction or rarefaction.	Combined compression and rarefaction.
12	46	46	56
12	40	42	56
10	25	27	36
9	32	20	30
9	32	29	46
6	16	15	24
3	12	13	17

W. S.

Lecture Experiments. By B. TOLLENS (*Deut. Chem. Ges. Ber.*, ix, 1540—1542).—*Decomposition of Glass by Boiling Water.*—Distilled water is boiled in a flask provided with two tubes, bent downwards a little above the cork, one of them made from ordinary glass, the other from combustion-tubing. A piece of delicate red litmus paper is unaltered by the steam issuing from the tubes, but if a drop of the condensed water in the tube of ordinary glass is allowed to fall on it, it becomes at once distinctly blue, while the water in the other tube produces no effect.

Demonstration of the Presence of Alcohol in Beer and Wine.—Wine or beer is heated to boiling in a flask fitted with a glass tube, $1\frac{1}{2}$ meter long, and 1 cm. wide. At first the water-vapour becomes condensed and runs back into the flask, but the zone of total condensation gradually rises till it reaches the top of the tube; if a light is then applied a flame of 10—20 cm. high may be obtained. Or the tube

may be bent downwards, and the first distillate lighted in a small capsule.

Ascent of Water caused by Evaporating Surfaces.—The pipe of a funnel is drawn out till the bore is reduced to a width of 1 mm. The funnel is then placed on a cylinder half filled with water, and of such a height that the pipe reaches close to the bottom. A piece of bladder is tied over the top of the funnel, which is then filled with water. The evaporation from the surface of the bladder causes water to rise up into the funnel, and the rise may be shown by a few drops of chloroform coloured with iodine, placed at the bottom of the cylinder. If the apparatus is exposed to a current of air (near an open window), the rise is very perceptible. G. T. A.

Inorganic Chemistry.

On the Purification of Hydrogen Gas for Analytical Purposes. By ERNST SCHOBIG (*J. prakt. Chem.* [2], xiv, 289—299).—The author has studied the action of a saturated solution of potassium permanganate in oxidising the gases which usually render hydrogen prepared from commercial zinc, impure. Whether the solution of permanganate is acid, alkaline, or neutral, a layer of pumice stone, 10 centimeters high, soaked in permanganate, was amply sufficient to remove every trace of arsenic, antimony, phosphorus, and carbon, from the hydrogen, even when it had been intentionally mixed with the compounds of these elements with hydrogen. The arsenic was oxidised to arsenic acid, the antimony to oxide and acid, the phosphorus to phosphoric acid, and the hydrocarbons to carbonic acid. The current of hydrogen was in every case moderately rapid.

The only peculiarity in testing for the oxidation products mentioned is the method of ascertaining if the gas is free from carbon. On passing the gas evolved from cast-iron and an acid through a red-hot tube, carbon was deposited; but not after the gas had been washed with permanganate. An acid or neutral solution of permanganate does not remove sulphuretted hydrogen from hydrogen. The solution must therefore be alkaline. The permanganate is reduced to manganate at a certain stage of the reaction. It is better, however, to lead the gas first through permanganate, to remove arseniuretted hydrogen, &c.; and then through soda to remove the sulphuretted hydrogen.

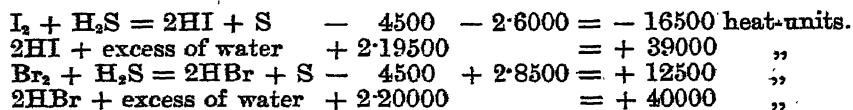
The author has also experimentally proved that pure hydrogen gas is slowly but completely oxidised by a solution of permanganate; and that it reduces silver nitrate even in the dark. W. R.

Preparation of Iodic Acid. By G. SODINI (*Gas. Chem. ital.*, vi, 321).—When this acid is prepared by passing chlorine into water containing suspended iodine, 20 parts of water to 1 of iodine must be

taken, in order to transform all the iodine into acid; otherwise chloride of iodine is formed. F. D. B.

Precipitated Sulphur. By M. SANSONI and C. CAPELLINI (*Gaz. Chim. ital.*, vi, 321).—Instead of acting on polysulphide of calcium with pure hydrochloric acid, the commercial acid free from arsenic is used; the precipitate collected and washed is again mixed with acid, and left for about an hour, shaking from time to time; the greyish colour then disappears suddenly; the acid is finally decanted, and used for a second operation. F. D. B.

Behaviour of Bromine and Sulphur Bromide to Sulphuretted Hydrogen. By A. NAUMANN (*Deut. Chem. Ges. Ber.*, ix, 1574—1577).—Bromine and iodine differ from each other in their action on sulphuretted hydrogen, as is shown by the different evolution of heat in each case. Thus:—



Iodine therefore and sulphuretted hydrogen can react on each other only in presence of water, till by the increasing amount of hydriodic acid in the water, the positive amount of the heat of absorption of the hydriodic acid has sunk from 39,000 to 16,500 units.

Dry sulphuretted hydrogen is decomposed by dry liquid bromine into hydrobromic acid gas and clear brown liquid sulphur bromide. This clear brown liquid, after the deposition of the sulphur, was found to contain—

While still saturated with HBr ..	77 per cent. of bromine.
After standing two days over lime ..	66 "
After several months	61 "

Sulphuretted hydrogen acts very slowly on this liquid, and finally produces a dark yellow solid mass, containing 18 per cent. of bromine saturated with HBr; after standing one day over lime (during which sulphur bromide escaped by sublimation), 9·6 per cent. of bromine.

The action of sulphuretted hydrogen on bromine dissolved in water is unlimited. After the liquid is saturated at the ordinary temperature with hydrobromic acid, the latter escapes in the gaseous state. The aqueous solution formed at ordinary temperatures contained in a cubic centimeter—

I. After the first violent reaction.....	1·06 gram of HBr.
II. After the addition of bromine, and when the solution had become colourless....	1·11 "
III. After further addition of bromine, and when again colourless	1·13 "

In the last case (III) 1 cubic centimeter at 20° weighed 1.762 grams, and contained—

Water	0.58 grams.	
Hydrobromic acid.....	1.13	„ = 64 per cent.
Sulphuric acid	0.052	„

The sulphur bromide from below the liquid in III contained when dry, 60 per cent. of bromine; after washing with water and standing for several days over lime and sulphuric acid, 56 per cent. of bromine.

A continual stream of hydrobromic acid gas and a concentrated solution of the same may therefore easily be prepared by passing sulphuretted hydrogen into a solution of bromine in water, till the water is saturated with hydrobromic acid gas; on further addition of sulphuretted hydrogen, the hydrobromic acid gas escapes, and may be absorbed by water in a receiver. The sulphur bromide may be decomposed by hot water, and the solution used again in the next operation to dissolve the bromine. The only drawback in the preparation of hydrobromic acid in this way is the formation of traces of sulphuric acid from the sulphur bromide.

Berthelot supposed that the limited action of sulphuretted hydrogen on iodine in presence of water is due to the formation of a definite hydrate, $\text{HI} + 4\text{H}_2\text{O}$. The author quoting Thomsen and others denies the existence of any such body at the ordinary temperature.

G. T. A.

On Boron. By W. HAMPE (*Liebig's Annalen*, clxxxiii, 75—101).—In 1857 Wöhler and Deville obtained, by heating aluminium with boric anhydride or amorphous boron, two classes of crystals, black and yellow, which were regarded by them, and have since been regarded, as varieties of crystallised boron. The author of the present paper, having repeatedly prepared and analysed these crystals, has arrived at the conclusion that they are not really boron, but compounds of that element with aluminium, or with aluminium and carbon.

The black crystals (Wöhler and Deville's graphitoidal boron) have been obtained by the author (1) by fusing aluminium with boric anhydride; (2) by fusing aluminium with boric anhydride, and cryolite or boric anhydride and fluor-spar; and (3) by passing boron fluoride over heated aluminium. Of these processes the first gave the best results, the most important condition for its success being the absence of carbon from the mixture. The temperature of melting iron, maintained for two or three hours, was found sufficient to produce the crystals, but the yield was larger at higher temperatures.

The crystals belong to the monoclinic system. They are black, or in very thin laminae dark-red, and yield a brownish-red powder. They have an extremely brilliant lustre, and when heated turn blue like steel, but they are nevertheless unalterable in oxygen at the temperature at which diamond burns easily. They are harder than corundum, but softer than diamond. Their sp. gr. is 2.5845, that of water at 17° being 1. The crystals are not attacked by hydrochloric acid or potash-ley, and only superficially by concentrated sulphuric acid, but are slowly dissolved by nitric acid. They are oxidised with incandescence

by fused potash or lead chromate, and slowly dissolved by fused acid potassium sulphate. When heated in the blowpipe flame on platinum they form with the metal an easily fusible alloy. Analyses of these crystals prepared at different times gave results agreeing very closely with the formula AlB_{12} .

The yellow crystals (Wöhler and Deville's diamond boron) were obtained by the author by heating aluminium with boric anhydride to the highest temperature obtainable in a wind-furnace, in crucibles lined with pure graphite, and allowing the fused mass to cool down very slowly. The crystals are quadratic, octohedrons being most common, but sometimes long prisms were obtained. They have a honey-yellow colour, which is a constant characteristic, and is not due, as Wöhler and Deville supposed, to impurities. They are somewhat easily broken, exhibiting a conchoidal fracture, and yield a honey-yellow powder. They are harder than corundum, but softer than diamond. In their behaviour with reagents they closely resemble the black crystals described above. Their sp. gr. is 2.615. The empirical formula of the crystals, as deduced from several closely concordant analyses, is $\text{C}_2\text{Al}_3\text{B}_{48}$, which may evidently be written $\text{C}_2\text{B}_{12} + 3\text{AlB}_{12}$, or $\text{Al}.\text{Al}.\text{B}_{24} + \text{Al}.\text{C}_2.\text{B}_{24}$, but it is by no means assumed that either of these latter formulæ represents the actual constitution of the compound.

All attempts to obtain pure crystallised boron have hitherto proved fruitless. J. R.

Phosphorus Oxybromochloride. By E. CHAMBERON (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 92—96).—1. *Decomposition by Heat.* Phosphorus oxybromochloride is gradually resolved by boiling into phosphorus oxybromide and oxychloride—a fact which explains why its boiling-point is not constant. The same decomposition is effected at once and completely by heating it to 185° in sealed tubes.

2. *Reaction with Phosphorous Acid.*—It has been shown by Geuther that phosphorus oxychloride reacts with phosphorous acid in the manner indicated by the equation—



By analogy, phosphorus oxybromochloride should react thus :

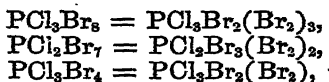


The author obtained, however, no phosphorus bromochloride, but instead of it a mixture of phosphorus tribromide and trichloride :



On the Constitution of Phosphorus Bromochlorides, and on "Molecular Compounds." By A. GEUTHER (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 128—140).—Some years ago Prinvaunt, and after him Michaelis, obtained, by the action of bromine on phosphorus trichloride, some new compounds, the principal of which agreed in composition with the formulæ PCl_3Br_3 , PCl_2Br_7 , PCl_3Br_4 . These

bodies were regarded by Michaelis as "molecular compounds" of phosphorus bromochloride with free bromine:



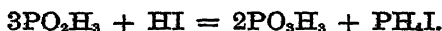
because, when subjected to the action of sulphur dioxide, they yielded free bromine, phosphorus oxychloride, and sulphur bromide, but no phosphorus oxybromide.

The author of the present paper points out that this conclusion of Michaelis is based upon the assumption that phosphorus oxybromide and bromine chloride do not react upon each other to form phosphorus oxychloride and free bromine. But he finds by direct experiment that this reaction does actually take place at moderate temperatures; so that in decompositions where phosphorus oxybromide and bromine chloride might be expected to be formed simultaneously, these products would not really be obtained, but instead of them their decomposition-products—phosphorus oxychloride and free bromine. Hence, he says the experiment of Michaelis is not conclusive as to the constitution of the compounds referred to.

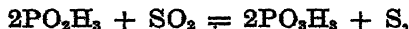
The remainder of the paper is occupied with a discussion of "molecular compounds" in general, which does not admit of abstraction.

J. R.

Hypophosphorous Acid. By A. L. PONNDORF (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 45–62).—1. *Action of Hydrogen Iodide.*—When perfectly dry hydrogen iodide is passed over hypophosphorous acid, a violent reaction takes place, accompanied by great rise of temperature. The products are phosphorous acid and phosphonium iodide:



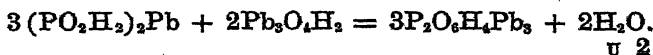
2. *Action of Sulphur Dioxide.*—Dry sulphur dioxide reacts with hypophosphorous acid in the manner indicated by the equation—



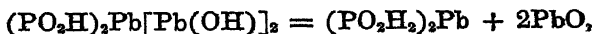
the principal products being phosphorous acid and free sulphur. At the same time, however, hydrogen sulphide is evolved, and some phosphoric acid is formed. The former of these bye-products is due, as the author found by direct experiment, to the action of free sulphur on hypophosphorous acid; and the latter to the action of sulphur dioxide on phosphorous acid at elevated temperatures.

3. *Nascent hydrogen* was found to be without action on either free hypophosphorous acid or its alkaline salts.

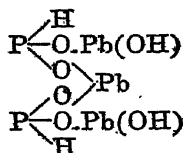
4. *Basicity of Hypophosphorous Acid.*—The author obtained, by boiling lead hypophosphite with lead hydrate ($\text{Pb}_2\text{O}_4\text{H}_2$), a salt crystallising in microscopic needles, and agreeing in composition with the empirical formula, $\text{P}_2\text{O}_5\text{H}_4\text{Pb}_2$. The formation of this salt is represented by the equation—



The composition of the salt is expressed by the formula—



and its constitution thus:



From the existence of this basic lead salt the author concludes that the phosphorus in hypophosphorous acid is trivalent, and not quinquivalent. The constitution of hypophosphorous acid is, therefore, analogous to that of phosphorous acid, and is expressed by the formula—



5. *Preparation of Ethyl Hypophosphite*.—The author attempted to obtain this substance (1) by the action of ethyl iodide on barium, lead, and sodium hypophosphites; (2) by the action of ethyl sulphide on lead hypophosphite; (3) by the action of a mixture of alcohol and sulphuric acid on sodium hypophosphite; (4) by the action of phosphorus on sodium ethylate; and (5) by the action of phosphorus biniodide sodium ethylate; but in every case without success.

J. R.

Constitution of Phosphorous and Hypophosphorous Acids.

By A. GEUTHER (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 116—127).—*Phosphorous Acid*.—The author contends that the conclusion arrived at by Michaelis, namely, that the phosphorus in phosphorous acid is quinquivalent, and not trivalent, is by no means borne out by the reactions cited in favour of that view.

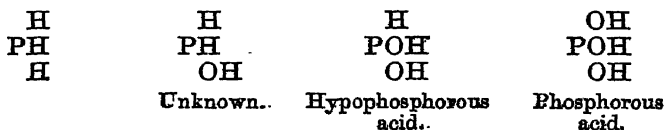
The most important objection to the formula $\text{P}(\text{OH})_3$ has been that of the three hydroxyl-groups contained in phosphorous acid, as thus represented, two only are readily exchangeable for metallic oxides, and not the third. And even now that Zimmermann has shown that sodium hydrate added in excess to phosphorous acid forms a salt insoluble in alcohol containing 3 atoms of sodium to 1 atom of phosphorus, thus establishing the existence of tribasic salts of this acid, it still remains to be seen why such salts are formed only with great difficulty. This difficulty in replacing the third hydroxyl-group is exhibited also in boric acid and in tribasic phosphoric acid. Now, since the neutral ethyl-compounds of boric, phosphoric, and phosphorous acids are all known, it follows that the difficulty of obtaining corresponding metallic derivatives is dependent on the nature of the metals. It may be said in general, that the tendency of a polybasic acid to exchange its hydroxyl-hydrogen for a metal decreases as the

number of hydroxyl-groups becomes diminished by substitution of metal for hydrogen.

According to the author the peculiar and anomalous behaviour of phosphorous acid, regarded as $P(OH)_3$, does not lie in the fact that its hydrogen is replaced by metals with difficulty, for in this respect it resembles all perhydroxyl-acids. It lies rather in the circumstance that the acid is not capable of passing into the monohydroxyl-acid, $PO(OH)$, by elimination of water, but breaks up into hydrogen phosphide and orthophosphoric acid.

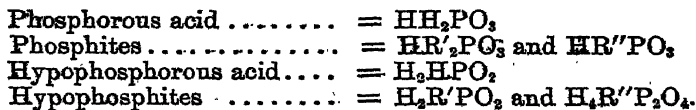
Hypophosphorous Acid.—This acid, assuming its formula to be $PH(OH)_2$, behaves in a similar manner to phosphorous acid, exchanging the hydrogen of only one of its hydroxyl-groups for metals. The same considerations apply to it as to phosphorous acid (see above).

Phosphorous and hypophosphorous acids may be regarded as being derived from hydrogen phosphide by oxidation in such a manner that the phosphorus remains trivalent, thus:



J. R.

Composition of the Phosphites. By C. RAMMELSBERG (*Deut. Chem. Ges. Ber.*, ix, 1577—1580).—According to Berzelius and Rose, the phosphites of lead and manganese contain one atom of phosphorus and one of hydrogen, while those of calcium, barium, and strontium contain two atoms of hydrogen to one of phosphorus. Others have assigned to barium phosphite the formula $H_4Ba_2P_2O_7$. The author is convinced from his experiments—direct estimation of the hydrogen, &c.—that the true composition of the phosphites and hypophosphites is:—



G. T. A.

Preparation of the Iodides of Potassium and Sodium, and of Potassium Bromide. By P. CHIAPPE and O. MALISCI (*Gazz. Chim. ital.*, vi, 320).—*Potassium Iodide.*—This salt, generally manufactured by heating caustic potash with iodine, is, as is well known, rendered impure by the presence of potassium iodate. In 1859 Professor Querri suggested that the potash might be replaced by potassium carbonate and the iodate reduced by means of ferrous iodide.

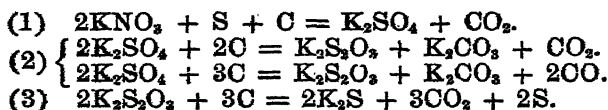
The authors show that if caustic potash be used, the reduction may be effected by means of iron, the free iodine forming ferrous iodide.

The method of preparation is as follows:—To the solution of potash at $30^\circ B.$, powdered iodine is added until the mass, rendered turbid by the deposition of iodate, remains slightly coloured, even after much

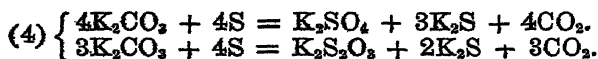
agitation; iron filings are then added, and the mixture is heated on a sand-bath. The reaction takes place rapidly, ferric oxide is precipitated, and carbonic anhydride evolved; when the reaction has ceased, the liquor is tested for iodate with a drop of hydrochloric acid, and more filings added, if it is still present. Finally, when the absence of iodate is certain, the ferrous iodide remaining is decomposed with potassium carbonate.

Sodium iodide and potassium bromide are prepared in a similar manner. F. D. B.

Potassium Thiosulphate. By M. BERTHELOT (*J. Pharm. Chim.* [4], xxiii, 247). Potassium thiosulphate has been assumed to be a constituent of the residue left after the explosion of gunpowder; and in very variable quantity, from 2 to 20 per cent., without apparent change in the conditions of explosion. Federow has given an ingenious explanation of its production, according to which the formation of sulphide and thiosulphate is due to the reduction by carbon of the potassium sulphate first formed,



as well as by the reduction of the carbonate by excess of sulphur:



The author has investigated the thermic formation of potassium thiosulphate, in order to verify these theories; he found the numbers negative, and their value too high to be compensated, even at a high temperature, by the difference of specific heats. According to Federow's equations, the formation of potassium thiosulphate would always be accompanied with an absorption of heat. The heat to be absorbed could be communicated only by the act of heating; but this heat produces a partial decomposition, accompanied by a great absorption of heat; it may, however, be followed by a reaction between the bodies formed. The best test is evidently to ascertain if the products formed are stable at the temperature to which they are exposed, or at least more stable than the original compound. In this special case the potassium thiosulphate ought to be stable at a temperature capable of decomposing potassium sulphate, or at least only dissociated to an analogous extent, in order to be able to exist to any appreciable amount after cooling. The same reasoning applies also to the transformation of the carbonate into thiosulphate.

The author has, therefore, determined the temperature to which potassium thiosulphate may be exposed without decomposing. It may be heated to 500° without sensible decomposition, but at a little above 550° it blackens and gives a mixture of polysulphide and sulphate, these



and at a still higher temperature sulphur volatilises from the polysulphide, which reaction evolves 27·7 heat-units at the ordinary temperature, and it evolves heat at the temperature at which the reaction begins, for, once commenced, the reaction continues of its own accord. From these considerations it follows that thiosulphate cannot be formed by explosion of powder. It is much more probable that it is produced from the polysulphides on exposure to air. Analyses of powder never give the amount of water. The oxygen absorbed by the polysulphide counterbalances this omission, and brings the sum of the constituents to 100.

W. R.

Chemical Constitution of Chloride of Lime. By C. STAHL-SCHMIDT (*Dingl. polyt. J.*, cexxi, 335—345).—Gay-Lussac represented chloride of lime by the formula CaOCl_2 , according to which pure chloride of lime should contain no calcium chloride. Göpner sought to establish this view by the assumption that chloride of lime, on treatment with dilute mineral acids, yields pure chlorine and no hypochlorous acid. This assumption has been proved untenable by Schorlemmer, who obtained hypochlorous acid by distilling with dilute nitric acid. Richters and Junker also contended that no calcium chloride is contained in chloride of lime, and this they sought to prove by boiling a solution of 1 gram of chloride of lime in 20 c.c. of a 20 per cent. phosphoric acid solution till all smell of chlorine had disappeared, and then finding no calcium chloride left. Thus they assumed that such a phosphoric acid solution cannot decompose calcium chloride on being boiled with it, and that only the chlorine of the compound CaOCl_2 is liberated. The author has, however, found that phosphoric acid solutions will decompose calcium chloride with liberation of hydrochloric acid. Kolb found that the richest chloride of lime he could prepare contained 38·72 per cent. actual chlorine, and this coincides with a formula $3(\text{CaO} \cdot \text{H}_2\text{O}) + 4\text{Cl}$ or $2(\text{CaO} \cdot \text{H}_2\text{O} \cdot \text{Cl}_2) + \text{CaO} \cdot \text{H}_2\text{O}$. This chloride of lime should be decomposed by water as follows:— $3(\text{CaO} \cdot \text{H}_2\text{O}) + 4\text{Cl} = \text{CaOH}_2\text{O}$ as a precipitate, and 2CaOCl_2 going into solution. Then the true constitution of the chloride of lime dissolved in water, as given by Ballard, should be:— $2\text{CaOCl}_2 = \text{CaOCl}_2\text{O} + \text{CaCl}_2$.

In a more recent publication Kolb gives to chloride of lime the formula $2(\text{CaOCl}_2) + \text{CaO} + 3\text{H}_2\text{O}$; the filtered solution consisted as before of CaOCl_2O and CaCl_2 . In the first formula Kolb assumes that water belongs to the constitution of chloride of lime, but afterwards he appears to forsake this view. According to Kolb also, three molecules of calcium hydrate are acted on by four atoms of chlorine to form chloride of lime, and thus far he and the author are agreed.

The author used in his experiments only chloride of lime which contained 39 per cent. of actual chlorine, and which had been formed exactly according to the formula $3\text{CaH}_2\text{O}_2 + 4\text{Cl}$. In a beaker a quantity of the above chloride of lime was treated with water, a trace of cobalt sulphate added, and the whole boiled; in this manner the calcium hypochlorite formed is converted, with liberation of oxygen, into calcium chlorate and calcium chloride without a trace of chlorine

escaping. The boiling is continued till a drop of the solution produces no coloration on iodised starch-paper. Carbonic acid is then passed into the solution for several hours, whereby the calcium hydrate separated at first is converted into calcium carbonate. Finally the whole is boiled for some time to drive off free carbonic acid, and separate any carbonate that may have been dissolved thereby. The precipitate was filtered, washed and weighed, and the amount of caustic lime therein calculated. This amount agreed well with the equation $2\text{CaHClO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O} = \text{CaCl}_2\text{O}_2 + \text{CaH}_2\text{O}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$.

The chloride of lime was next treated with freshly-prepared sulphurous acid, quite free from sulphuric acid, until the reaction with iodised paper ceased. Thus two molecules of sulphurous acid were converted into sulphuric acid by one molecule of hypochlorous acid, and this united with an equivalent quantity of lime, setting free a corresponding proportion of hydrochloric acid. The whole was then evaporated on the water-bath to dryness, when the free hydrochloric acid escaped and sulphate of lime remained, together with the one molecule of calcium chloride originally existing in the dry chloride of lime.

$\text{CaCl}_2\text{O}_2 + \text{CaH}_2\text{O}_2 + \text{CaCl}_2 + 2\text{SO}_2 = 2\text{CaSO}_4 + 2\text{HCl} + \text{CaCl}_2$. The calcium chloride was then estimated with silver solution. The results agreed well with the formula quoted.

The behaviour of chloride of lime at high temperatures was next tested. It is already known that chloride of lime, under the influence of heat, decomposes with formation of calcium chloride and chlorate and liberation of oxygen gas and sometimes of chlorine. With a less intense heat, according to Morin, one-third of the calcium hypochlorite passes into chloride and chlorate, whilst two-thirds remain unaltered, and then a stronger heat decomposes this into calcium chloride and oxygen.

When freshly prepared chloride of lime is heated in a bulb-tube between 100° and 120° , water and chlorine escape. When the temperature rises, no more chlorine escapes after a certain point, but at and above 300° pure oxygen is liberated. When an incipient red-heat is attained, the whole melts to a fluid mass, clear and transparent as water, resembling fused nitre, and on cooling solidifies to a crystalline mass, resembling the latter salt in appearance under like conditions. At a red-heat a further liberation of gas takes place, and the mass then becomes muddy, opaque and thick, with separation of an insoluble compound. By heating chloride of lime, all the chlorine which escapes does so as chlorine, not a trace as hydrochloric acid.

For the estimation of the water in chloride of lime, a portion of the body was heated in a bulb-tube, first slowly, and then afterwards to ignition, a current of dry air, free from carbon dioxide, being passed over it, and the water escaping being retained by a calcium-chloride tube.

The amount of water thus estimated agreed very well with the formula $2\text{CaClHO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$. It appears then that this final molecule of water is not liberated even at a red-heat.

Another portion of the chloride of lime is now mixed with dry,

ignited sodium carbonate, and the whole ignited in the bulb-tube, so that the mass does not quite fuse. Three molecules of water are thus set free, with simultaneous formation of calcium carbonate, sodium chloride, and free oxygen. The numbers obtained completely bear out the formula $2\text{CaHClO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$.

By the first heating 9.96 per cent. of water escaped, and by the second 5.04 per cent.: total 15 per cent.

It was finally discovered that by heating chloride of lime to 120° 4.6 per cent. of chlorine were given off, and by further heating over the lamp 10.85 and 11.60 per cent. Under these circumstances also 9.89 per cent. of water and some oxygen were liberated. At first then there are liberated from one molecule of chloride of lime, besides the $2\text{H}_2\text{O}$, also $1\text{Cl} + 1\text{O}$, and further by stronger heating $\frac{1}{2}\text{O}$ follows.

The loss for the $2\text{H}_2\text{O}$	=	9.89	per cent.	} 24.03 per cent.
" " 1Cl	=	9.75	"	
" " 1O	=	4.39	"	
" " $\frac{1}{2}\text{O}$	=	2.19	"	
Total loss				= 26.22

A portion of the chloride was now ignited, the residue dissolved in water, and the amounts of calcium hydrate and calcium chloride determined.

The results agreed sufficiently well with the formula mentioned. 100 parts of chloride of lime contain according to the formula 19.23 per cent. of lime (CaO) and 53.36 per cent. of calcium chloride. Results obtained:—Lime, 18.83 and 18.11 per cent; calcium chloride, 51.00 and 52.24 per cent.

It is now shown that if the actual compound in chloride of lime were CaOCl_2 , as according to Göpner, then by necessity it must have been formed as follows:— $3\text{CaH}_2\text{O}_2 + 4\text{Cl} = 2\text{CaOCl}_2 + \text{CaH}_2\text{O}_2 + 2\text{H}_2\text{O}$. But this formula fails to explain several of the results obtained by the author, and chiefly that by which it appears that the third molecule of water is obstinately retained in the compound, for had it been contained as calcium hydrate merely, the strong heating would have driven it forth. Göpner's formula does not in any way account for the fusibility of the chloride of lime to a clear glassy mass at a moderately high temperature. A mixture of calcium hydrate, calcium chloride, and calcium chlorate does not possess this property. It is considered, therefore, that chloride of lime contains no calcium hydrate. Finally, the author considers it as proved, that chloride of lime has a constitution expressed by the formula $2\text{CaHClO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$. He also joins Fresenius in the view, that the calcium chloride in this formula must be considered as standing outside the constitution of the chloride of lime.

Whether the formula CaHClO_2 or $\text{Ca} \begin{matrix} \text{OH} \\ \diagup \\ \text{OCl} \end{matrix}$ gives the true situation of the atoms in the compound, or whether this formula should be doubled, the author will not decide. He contents himself with proving

that the bleaching compound arises by the replacement of an atom of hydrogen in calcium hydrate by an atom of chlorine, and that this hydrogen is contained in chemical combination. Finally that the compound should be regarded as a *calcium hydro-oxychloride*.

W. S.

Zinc Hydride. Reduction of Silver Nitrate by Hydrogen. By A. R. LEEDS (*Deut. Chem. Ges. Ber.*, ix, 1456—1459).—The hydrogen obtained by acting with pure dilute sulphuric acid on the zinc of the Passaic Zinc Company contains a trace of zinc and burns with a blue flame. On purifying it by a solution of silver nitrate, not only silver separated out as a grey powder, but in the upper part of the U-tube nearest the hydrogen apparatus crystals of silver nitrite had formed. When hydrogen, after being passed through an acid solution of ferrous sulphate, concentrated sulphuric acid, and over pure potash is passed through a solution of pure silver nitrate, the quantity of silver precipitated is almost proportional to the time, and the reduction commences as soon as the air is replaced by hydrogen.

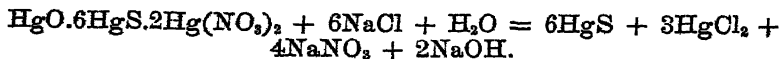
C. S.

Action of Nitric Acid on Mercuric Sulphide. By FREDERICK GRAMP (*J. prakt. Chem.* [2], xiv, 299—304).—The various compounds obtained by the action of nitric acid on mercuric sulphide are:—

1. $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}$: prepared by Barfoed, by boiling black mercuric sulphide for 24 hours with nitric acid of 1.52 specific gravity.

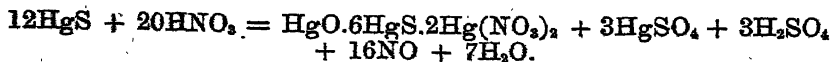
2. Mercuric sulphate, obtained by the author on heating cinnabar to 120° in a sealed tube with nitric acid of 1.4.

3. A new compound, of the formula $\text{HgO} \cdot 6\text{HgS} \cdot 2\text{Hg}(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O}$, obtained by heating cinnabar, or better, the black sulphide with nitric acid of 1.2 specific gravity to 120° in a sealed tube. It forms a white crystalline powder insoluble in water and in nitric acid of 1.2 specific gravity. When treated with sodium chloride the following reaction takes place:—



This reaction was confirmed experimentally by ascertaining the amount of sulphide and chloride of mercury formed.

The reaction expressing its formation is—



The compound crystallises with 12 molecules of water, 7 of which it loses at 150° .

W. R.

On the Atomic Weights of the Metals of the Cerium-group. By C. RAMMELSBERG (*Deut. Chem. Ges. Ber.*, ix, 1580—1583). The determination of the specific heats of cerium, didymium, and lanthanum by Hillebrand has proved that the atomic weights of these

three metals (and probably also of the others of this group) are $1\frac{1}{2}$ times larger than those hitherto used. The author has, therefore, recalculated the composition of the minerals in which these metals occur, and gives a table of them, together with the old formulæ.

C. S.

Solubility of Lead Carbonate in Ammonium Butyrate. By A. BERTRAND (*J. Pharm. Chim.* [4], xxiii, 345—346).—At the temperature of 10°C ., 100 grams of neutral ammonium butyrate dissolve 1.038 gram of lead carbonate in six minutes, and 1.536 gram in four days. The solution is limpid and colourless, and might prove a means of obtaining lead carbonate in crystals.

R. R.

Preparation of Pure Bismuth and Bismuth Compounds. By HANS THÜRACH (*J. prakt. Chem.* [2], xiv, 309—316).—The usual impurities, even in what is sold as pure bismuth, are silver and iron. Quesneville's process, viz., fusing the metal with nitre, has the disadvantage of being extremely wasteful, a large quantity of bismuth being oxidised. Nor can bismuth be separated from it by precipitation as oxychloride with water, for iron is invariably a constituent of the precipitate. If the bismuth be fused under a mixture of potassium chlorate and a little sodium carbonate, the iron is completely oxidised, while very little bismuth is lost: for the fused mass does not become alkaline as is the case when nitre is used as flux; 2 to 5 per cent. of sodium carbonate should be added, and the fusion should last for a quarter of an hour. No method of separating bismuth from iron by the wet method was successful, except by crystallising the double chloride of bismuth and the alkalis, and by precipitating the bismuth from a slightly acid solution with oxalic acid. The bismuth oxalate, $\text{Bi}_2(\text{C}_2\text{O}_4)_3 + 15\text{H}_2\text{O}$ comes down absolutely free from iron. Too large an excess of oxalic acid should be avoided, for the oxalate is slightly soluble in the acid; the precipitate should not be allowed to stand too long in contact with water, else the basic oxide is formed which retains the iron. The oxalate in ignition yields metallic bismuth.

This process has not been attempted quantitatively.

The only method of separating silver from bismuth is to oxidise the bismuth and leave metallic silver.

Bismuth is best precipitated as sulphide. The liquid is then warmed, and the sulphide cakes together, and may be easily filtered and washed. On ignition in air it is converted into bismuth oxide, and may be weighed as such.

W. R.

A Compound of Chromium and Arsenic. By R. H. C. NEVILLE (*Chem. News*, xxxiv, 220).—Prepared by pouring a hot strong solution of chromic anhydride into a hot solution of arsenious acid, and kept at the boiling point for some time. It forms a dark green powder, and has the formula of an arsenite of chromium, CrAsO_3 .

W. R.

Method of Preparing Ferric and Cupric Oxides from the Sulphates, so as not to obtain Basic Sulphates. By A. SOLDAINI (*Gazz. Chem. ital.*, vi, 324).—When ferric sulphate is decomposed by

sodium carbonate, even in excess, the washed precipitate always contains sulphuric acid, or consists wholly or partly of basic sulphates. In this state they are far less soluble and are unadapted to the production of iron reduced by hydrogen, or indeed by any other pure product. This is avoided by pouring the ferric sulphate into a solution of the carbonate maintained in excess.

As regards the copper salt, it appears that, by heating a solution of cupric sulphate in excess with potash, a light blue precipitate is obtained, formed by the union of a molecule of sulphate with two of oxide.

F. D. B.

Mineralogical Chemistry.

Atacamite. By T. C. CLOUD (*Chem. News*, xxxiv, 254).—This mineral is found in large quantities and often in magnificent specimens, and in many cases it is evident that it has been formed from the oxide, most probably by the action of salt water. When it occurs in contact with limestone rock near the surface of the ground, it is partly or wholly converted into green carbonate of copper.

Analysis of a well-crystallised specimen :—

Cu.	Cl.	CuO.	Insoluble residue.	H ₂ O by difference.
13.73	15.38	55.91	1.47	13.51 = 100.00

The crystals selected for analysis were about $\frac{1}{4}$ -inch long, of a clear, dark-green colour, and quite transparent. The reaction which takes place when oxychloride of copper is heated with access of air is the following :—



At the cooler part of the combustion tube, cuprous chloride had formed a sublimate, while in place of the original substance there remained a brilliant black fritted mass of cupric oxide.

D. B.

Cinnabar from Oregon. By C. W. DABNEY (*Chem. News*, xxxiv, 180).—The specimen was in calcite from Oregon; it evolved sulphuretted hydrogen on treatment with dilute hydrochloric acid. The results of analyses were :—

Hg.	S.*	Fe.	SiO ₂ .	O (by diff.).
78.42	14.13	4.09	3.06	0.30 = 100

Assuming that the mercury all exists as HgS, that the sulphur, which was given off as H₂S exists as FeS₂ (magnetic pyrites), and the residue as FeS₂, the following numbers are obtained :—

* Given off as SH₂ 0.54; in the residue 13.59.

HgS.	Fe ₇ S ₈ .	FeS ₂ .	Fe ₂ O ₃ .	SiO ₂ .
90·97	1·37	1·95	3·36	3·06 = 100·71
				M. M. P. M.

A New Nickel Mineral from New Caledonia. By P. G. W. TYPKH (*Chem. News*, xxxiv, 193).—This mineral has been already examined by Liversidge (this Journal, xii, 613). The author's results are somewhat different from those of Liversidge. The mineral could be separated into two parts, of apple-green and dark green colour respectively, the former constituting the greater part of the ore. The percentage composition of the green substance, after drying at 100°, was as follows:—

Water lost on ignition.....	= 7·510
Silica.....	55·900
Nickel oxide.....	35·565
Alumina and ferric oxide.....	0·825
Lime.....	traces.
Magnesia.....	0·810
	<hr/> 100·610

The composition is approximately that of a hydrated nickel disilicate, Si₂O₆NiH₂.

Another portion yielded somewhat different results. The author regards the mineral as probably the result of the action of hydrated silicic acid upon some nickel-compound, and he thinks that the proportions of silica and nickel oxide vary so much that no mineralogical formula can be given.

M. M. P. M.

Pyrrhotite from Elizabethtown, Ontario. By B. J. HARBINGTON (*Am. J. of Sci.* [3], xi, 387).—The following is the analysis of a crystal:—Iron, 60·560; copper, 0·145; manganese, 0·060; nickel, 0·112; cobalt, 0·111; sulphur, 39·020; silica, 0·036. Hardness between 3½ and 4. Specific gravity, 4·622. Readily attracted by the magnet and possessing polarity.

R. R.

On Substances which accompany Molybdenum Glance. By HANS THÜRACH (*J. prakt. Chem.* [2], xiv, 305—309).—It is well known that molybdenum ochre commonly accompanies molybdenum glance. The author has examined a number of specimens of that mineral, in order to ascertain what compounds are formed during its decomposition by exposure to air and moisture. Among these he found free molybdic acid, which was extracted with cold water, and recognised as free by its action on litmus and turmeric papers; lime, strontia, magnesia, ferrous oxide, and sulphuric acid were also extracted with cold water. The residue, boiled with hot water, yielded calcium molybdate, together with traces of calcium, iron, and sulphuric acid. Dilute hydrochloric acid gave a similar extract, and strong acid dissolved small quantities of copper and bismuth, besides iron, aluminum,

calcium, strontium, and traces of magnesium and sulphuric acid. The residue was oxidised with nitric acid, leaving silica.

The presence of free molybdic acid and sulphates is explicable by the oxidation of the glance in the neighbourhood of dolomite, the magnesium sulphate being removed, owing to its solubility. Hydrochloric acid removes all foreign substances, except silica, from molybdenum glance; the glance is best decomposed by nitric acid of 1·3 or 1·4 specific gravity. Bromine is without action on it, and to decompose it by roasting is a slow operation, which, however, may be greatly accelerated by adding ammonium nitrate. The residue is then free from sulphur.

W. R.

Durangite. By G. J. BRUSH (*Am. J. of Sci.* [3], xi, 464, 465).—Analysis of some crystals of the mineral, darker in colour than those previously examined by the author, gave the following results:—Arsenic acid, 53·11; alumina, 17·19; ferric oxide, 9·23; manganic oxide, 2·08; soda, 13·06; lithia, 0·65; fluorine, 7·67. The mineral is, therefore, analogous in chemical composition to amblygonite, and its formula may be written $(\text{Na}, \text{Li})_2(\text{Al}, \text{Fe}, \text{Mn})\text{As}_2(\text{O}, \text{F})_6$.

R. R.

The Rocks of the "Chloritic Formation" on the Western Border of the New Haven Region. By G. W. HAWES (*Am. J. of Sci.* [3], 122—126).—These rocks represent pyroxenic igneous rocks, but, according to Dana, they are undoubtedly of metamorphic origin. The analyses of three specimens are detailed. To these rocks the names *metadolerite*, *metadiabase*, and *metamelaphyre* are given, in accordance with Dana's suggestion.

	Metadolerite.	Meta- diabase.	Porphyritic metadiabase.	Meta- melaphyre.
SiO_2	50·36	48·20	48·61	55·07
Al_2O_3	14·57	14·12	17·81	14·18
Fe_2O_3	2·48	2·00	0·25	7·20
FeO	8·31	7·41	8·46	1·92
MnO	0·46	1·24	0·20	0·30
CaO	11·13	11·50	11·16	9·03
MgO	7·62	8·19	7·76	5·98
Na_2O	3·04	2·60	2·77	4·11
K_2O	0·44	0·23	0·47	0·37
TiO_2	1·70	—	—	—
Cr_2O_3	trace	1·58	1·35	1·56
Loss on ignition	0·78	water 2·20	1·63	0·72
	<hr/> 100·89	<hr/> 99·27	<hr/> 100·47	<hr/> 100·44
Specific gravity	3·04	3·01	3·01	2·99

The metadolerite, when cut in thin sections, is evidently composed of pyroxene, a triclinic felspar, and titanite ironstone.

The metadiabase is a mixture of pyroxene, chlorite, labradorite, and titanite ironstone. The rock in places contains pyrite. The absence of calcium carbonate is noticeable.

In the porphyritic metadiabase the presence of those minerals which

are usually contained* in the more compact varieties, may be recognised under the microscope.

Metamelaphyre appears to be a mixture of pyroxene and oligoclase.

M. M. P. M.

Analysis of the Ash of Lignite. (*Dingl. polyt. J.*, cccxii, 188—189.)—The following analysis made by E. Schulze, gives the composition of the ash of lignite from Dorheim, in Hessa, from which it is seen that the amount of potash and phosphoric acid is but very small:—

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	H ₂ SO ₄ .
0·46	0·34	11·40	2·10	5·08	22·6	6·40
H ₃ PO ₄ .		CO ₂ .	SiO ₂ , sand, and clay.			
0·66		0·60	49·58 = 100·00 per cent.			

D. B.

Gas-wells in Pennsylvania. By J. LAWRENCE SMITH (*Ann. Chim. Phys.* [5], viii, 566).—The principal wells are found in Butler Co., Pennsylvania, lat. 40° 30', long. 80°; wells of minor importance are also found in the neighbouring counties. The two most productive wells are those of Burns and Delamater, about 30 miles from Pittsburgh. Their depth is about 1,600 feet, for they are bored down to the fourth layer of sand. The Burns well has never given oil, but the one at Delamater was a petroleum well, of 1,600 litres; it now gives gas at such a pressure that plummet-lines weighing 800 kilos. can be drawn out of it with the hand.

The Delameter well is situated in a valley surrounded by mountains, and furnishes heat and light to the whole neighbourhood. A large number of pipes diverge from this well; one conducts the gas direct to the cylinder of an engine which, with this pressure alone, acquires an enormous speed. Another pipe feeds a flame capable of reducing as much iron ore as half the blast furnaces of Pittsburgh can put out in a day. 20 yards further on is the main pipe of the wells; from a pipe 3 inches in diameter issues a flame 40 feet high, the noise of which shakes the hills. For a distance of 50 feet round, the earth is burnt; but, further off, the vegetation is tropical, and enjoys a perpetual summer.

On a calm night the noise can be heard at a distance of fifteen miles; at four miles the noise is like that of a train passing near, whilst close by it resembles that of a thousand locomotives blowing off steam. At the distance of a furlong, the noise is like the continued roar of artillery, the human voice can scarcely be heard, and the flame reaches a height of 70 feet. In winter the surrounding mountains are covered with snow, but on two acres around the well the grass is green, except in the immediate neighbourhood, where the soil resembles lava.

The composition and pressure of the gas have been determined with great care by Wath. It is almost entirely composed of ethane, C₂H₆, with a small quantity of carbon monoxide and dioxide. Its illuminating

power is equal to that of $7\frac{1}{2}$ candles, that of coal gas being 16. Its heating power is 25 per cent. greater than that of good bituminous coal. At the well, in a $5\frac{1}{2}$ inch pipe, the pressure is 100 lbs. per square inch; in a smaller pipe it is more than 200 lbs. per square inch.

The ascending speed of the gas is 1,700 feet per second, and the yield is, in round numbers, one million cubic feet per hour. The daily yield of gas is thus about 1,408 tons.

Some of these wells have given gas for twelve years, and the yield is still undiminished; a well at Fairview has fed more than 100 engines for five years, and the production is at present the same as on the first day.

The gas is used in several blast-furnaces with great advantage. It is also used for puddling the iron, and is said not to injure the furnace so much as coal. It is also used for ordinary heating and lighting purposes in several towns. The gas from four of the wells has been analysed by S. P. Sadler, with the following results:—

	Burns, Butler Co.	Lechburg, Westmoreland Co.	Harvey, Butler Co.	Cherry Tree, Indiana Co.
CO ₂ ..	0.34	0.35	0.66	2.21
CO	trace	0.26	—	—
CH ₄ ..	75.44	89.65	80.11	60.27
C ₂ H ₄ ..	18.12	4.39	5.72	—
C ₂ H ₆ ..	—	0.56	—	—
H	6.10	4.79	13.50	22.50
O	—	—	—	0.83
N	—	—	—	7.32
	100.00	100.00	99.99	93.13

The density of the gas from the Burns Well was found to be 0.698.

C. W. W.

Foreign Bodies in Snow. By M. BOUDIER (*J. Pharm. Chim.* [4], xxiii, 340—345).—Of the solid matters floating in the air, and retained by the snow, the most abundant was found to be soot; next came cells of *Protococcus viridis*, and spores and filaments of other cryptogams; then granules of starch, and cells and fibres of various plants. Epithelial cells, and hairs of animals were also present, as well as fibres of wool and silk. These last being dyed, indicated the presence of man, as did also the fibres of hemp, cotton, and indigo. The amount of foreign matter was greatest in the snow collected at the lowest levels, especially in the vicinity of human habitations and of woods, which are both fertile sources of floating particles. Potassium permanganate was used to estimate the amount of organic dissolved matter retained by the filtered snow-water.

Intimately mixed with the soot were the ferruginous corpuscles observed by Tissandier. These are regarded by the author, in opposition to the opinion of Tissandier, as of terrestrial origin. R. R.

Carbon Compounds in Meteorites. By J. L. SMITH (*Am. J. Sci.* [3], xi, 388—395, and 433—442).—The graphites which occur in nodular concretions in the iron meteorites of Sevier County,

De Kalb County, and Cranbourne, were treated by the author with fuming nitric acid and potassium chlorate, and were found to yield the same graphitic oxide which Brodie in 1860 showed to be the product of the reaction with terrestrial graphite. The meteoric graphite is, however, more readily oxidised than ordinary graphite. It burns in the air with great difficulty, but very easily in oxygen, leaving a small proportion of ash. The meteoric graphite was finely powdered, and treated for some hours with ether; the ether, filtered off and allowed to evaporate slowly, was found to leave long, colourless, acicular crystals, together with some rhomboidal crystals and rounded particles. This residue had a peculiar aromatic and somewhat alliaceous odour. Heated on a piece of platinum foil, the crystals fused at about 120° , and when heated in a tube, they first melted and then volatilised, condensing into yellow drops which soon solidified, leaving a carbonaceous residue. The crystals were insoluble in alcohol, but very soluble in carbon bisulphide. Fuming nitric acid oxidised them, giving sulphuric acid as one of the products. The powdered graphite which had been exhausted by ether, yielded to sulphide of carbon other soluble matter: for the evaporated filtrate left a yellow solid, which fused when heated on platinum foil; then sulphur was burnt off, and carbonaceous matter was left. The yellow solid when heated in a tube, sublimed, leaving a black residue.

The author also obtained for examination portions of two out of the only four known stony meteorites in which carbon is disseminated throughout the mass, namely, that which fell at Alais, in 1806, and that at Orgueil, in 1864. Small quantities of these, finely powdered, boiled with water, dried, and treated successively with ether and carbon bisulphide, yielded the same crystals and yellow mass as the meteoric graphite. An analysis of the acicular crystals gave:—Sulphur, 79.25; carbon, 15.00; hydrogen, 3.00; but, from the minuteness of the quantity of the material employed, these figures cannot be much relied on.

R. R.

The Gases contained in Meteorites. By A. W. WRIGHT (*Am. J. of Sci.* [3], xi, 253—262).—Many analyses of gases evolved from meteorites belonging to the two classes "iron" and "stony" are detailed. The methods employed are also described. The general result is that there is a marked difference between the gases given off from "stony" and those from "iron" meteorites. The former yield much larger volumes of gas at low temperatures, and the percentage amount of carbon dioxide in this gas is very much greater than in the gas evolved from iron meteorites. The carbon dioxide from the iron meteorites examined never exceeded 15 p. c. of the total volume of gas; fully 50 p. c. of the gas evolved from the stony meteorites, when heated to redness, consisted of carbon dioxide; at 350° carbon dioxide constituted from 80 to 90 p. c. of the total gas, and at 100° , 95 p. c.

The percentage amount of carbon monoxide evolved is much greater in the case of iron than in the case of stony meteorites. The gas from the latter meteorites appeared also to contain small quantities of marsh-gas.

The author supposes that the carbon dioxide is condensed upon, as well as absorbed by, the fine particles of iron, and that the readiness with which it is given up is then to be accounted for. The gases from the stony meteorites which were examined spectroscopically gave cometary spectra.

M. M. P. M.

The Meteoric Stone of Waconda, Mitchel County, Kansas. By C. U. SHEPARD (*Am. J. of Sci.* [3], xi, 473—474).—The stone, of which some fragments were examined by the author, was found two years ago, lying in the grass on the slope of a ravine, two miles from Waconda. There is much amorphous, whitish matter, among which very minute, rounded, lustrous grains of nickeliferous iron are thickly scattered; while troilite (magnetic pyrites) occasionally presents itself in larger grains, or in aggregations of imperfect crystals. The crust is much crumpled or reticulated, and of a brownish, iron-black colour. The earthy portion was in part decomposed by aqua regia, yielding magnesia, ferrous oxide, and lime, in the proportions usual in chrysolite. The specific gravity of a fragment free from crust was 3.58.

R. R.

Organic Chemistry.

Selenium Compounds of Ethyl. By L. V. PIEVERLING (*Deut. Chem. Ges. Ber.*, ix, 1469—1471).—*Diethyl Monoselenide*, $(C_2H_5)_2S$, is obtained pure only by distilling phosphorus pentaselenide with equivalent quantities of potassium ethylsulphate and caustic potash, and not too much water. It is a liquid having an alliaceous but not disagreeable smell, and boiling at 108° . It combines gradually with ethyl iodide to $Se(C_2H_5)_2I$, crystallising in white needles, which are readily soluble in water. Between 86° — 126° it splits up, and by treating it with moist silver oxide, it is converted into the hydroxide, $Se(C_2H_5)_2OH$, which is as alkaline as caustic potash, and could not be obtained in a solid state. Its salts crystallise, and have an alliaceous odour, and a bitter and pungent taste. The acid tartrate, $Se(C_2H_5)_2C_4H_4O_6 + 2H_2O$, forms pale pink needles. $2Se(C_2H_5)_2Cl + PtCl_4$ is a crystalline precipitate, crystallising from hot water in brilliant, red-pointed rhombohedra.

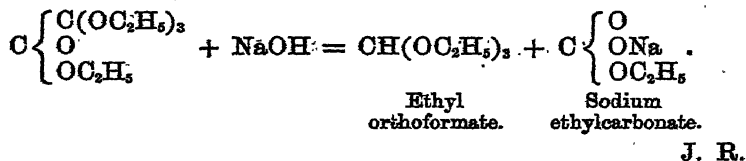
G. S.

Action of Bromine on Sodium Ethylate. By M. BARTH (*Deut. Chem. Ges. Ber.*, ix, 1455—1456).—When bromine vapour acts on pure sodium ethylate, dried at 180° , it forms acetic ether, hydrobromic acid, bromal, ethyl bromide, sodium bromide, and a little bromate.

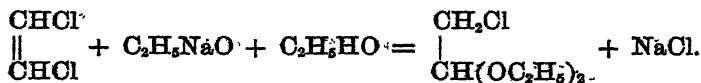
C. S.

Action of Sodium Ethylate on Trichloroacetic Acid. By G.

KLIEN (*J. Zeitschr. f. Naturw.*, x, 63—66).—The author caused ethyl trichloracetate and sodium ethylate to act upon each other under various conditions, in the hope of obtaining the ethyl-derivative of triethyloxalic acid, but without success, this substance apparently breaking up, under the influence of the alkali present, in the manner indicated by the following equation :—



Preparation of Monochlorodiethoxyethane. By G. KLIEN (*J. Zeitschr. f. Naturw.*, x, 67—69).—The author has obtained this substance by the action of alcoholic sodium ethylate on dichlorethene at elevated temperatures. The reaction is represented thus :—



Monochlorodiethoxyethane is a colourless, oily liquid, of peculiar aromatic odour, boiling at 155°. Its sp. gr. is 1.026 at 15°.

J. R.

A Polymeride of Ethene Oxide. By A. WURTZ (*Compt. rend.*, lxxxiii, 1141).—Some ethene oxide having been left in a sealed tube, was found a year after to have solidified into a white crystalline mass melting at 56°. Heated in a tube it volatilised with partial decomposition, and the vapour condensed into a semi-solid mass. It was neutral, tasteless, and very soluble in water and alcohol, less so in ether, which, however, dissolved it on heating, and deposited the greater portion again on cooling. The solutions leave, on evaporation, a crystalline, laminated, and very light body. The aqueous solution does not reduce copper. This substance has the composition of ethene oxide, and is probably a polymeric modification of that body.

C. W. W.

On Epichlorhydrin. By E. LAUFER (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 141—152).—The author has attempted to replace the chlorine in epichlorhydrin by monatomic alcoholic or acid radicles. With this view he acted upon it with sodium ethylate free from alcohol, potassium acetate, and silver acetate. The results showed that no simple glycid-derivatives are obtained by the replacement of chlorine by monatomic radicles, but that, for the most part, derivatives of glycerin are formed, owing to secondary decomposition.

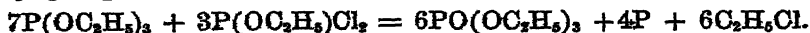
J. R.

Action of Ethoxyl-compounds of Phosphorus on Phosphorus Chlorides and Phosphorous Acid. By E. CHAMBON (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 97—103).—1. *Ethyl Phosphite and Phosphorus Trichloride*.—These substances react upon each other to form monethylphosphorous chloride (phosphorus oxethylchloride), in accordance with the equation—



but the product of this reaction is further acted on by the ethyl phosphite present, as is seen in the following experiment.

2. *Ethyl Phosphite and Phosphorus Oxethylchloride*.—When these bodies are mixed together in molecular proportions and gradually heated to 120°, ethyl chloride is given off, whilst free phosphorus and ethyl phosphate are left behind—



3. *Ethyl phosphite and phosphorous acid* do not act upon each other at 200°.

4. *Phosphorus oxethylchloride and phosphorous acid* when heated together evolve ethyl chloride and hydrogen chloride, free phosphorus and phosphoric acid remaining in the retort—



5. *Phosphorus oxethylchloride and phosphorus trichloride* do not act upon each other even when boiled together.

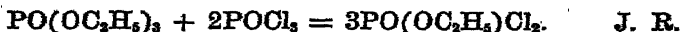
6. *Phosphorus oxethylchloride* when heated to 165° in a sealed tube is resolved into ethyl chloride, phosphorus trichloride, free phosphorus, and phosphoric anhydride—



7. *Phosphorus oxethyloxychloride (monethylphosphoric chloride)* when heated to 140° in sealed tubes is resolved into ethyl chloride, phosphorus oxychloride, and phosphoric anhydride—



8. *Ethyl phosphate and phosphorus oxychloride* when heated to 110° in a sealed tube combine together to form phosphorus oxethyloxychloride, in accordance with the equation—



Inactive Fermentation Amylic Alcohol. By L. BALBIANO (*Gazzetta chimica italiana*, vi, 229—239).—The method employed for obtaining this alcohol was founded on Pasteur's discovery of the comparative insolubility of the barium salt of the acid amyl sulphate derived from the inactive alcohol. In preparing the acid amyl sulphate from the mixed alcohols, it was found that the portion of the alcohol which was not acted on had the same rotatory power as the original, thus confirming Le Bel's statements on this subject. The mixed barium salts were separated by fractional crystallisation, which had to be performed from 18 to 20 times before the salt from the inactive

alcohol presented the constant solubility at 10° of 9·7 parts in 100 of water. Fermentation butylic alcohol was also converted into valeric acid and then into amylic alcohol in the ordinary way. This synthetically formed alcohol yielded a barium amylsulphate having precisely the same degree of solubility as that of the salt obtained from the inactive amylic alcohol, so that there can be but little doubt that the inactive alcohol is strictly homologous with fermentation butylic alcohol, and has the constitution represented by the formula $\text{CH}_3\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}_2(\text{OH})$.

The pure inactive amylic alcohol was obtained from the barium salt by digesting it for several hours with a slight excess of dilute sulphuric acid, and then distilling, when the whole of the alcohol passed over with the first portions of the distillate. When dried it is a colourless liquid, which has no perceptible action on polarised light in a column 40 meters long. It boils at 131·4° with the thermometer in the vapour, and under a pressure of 747 mm. reduced to 0°. Its density at 0° is ·8238. It dissolves in about 50 volumes of water at 14°, and the solution becomes milky when heated to 50°. It was found that neither the pure inactive alcohol nor the crude mixture of amylic alcohols was altered when heated to 250° either in the dry state or in the presence of water.

The *amyl chloride* prepared by heating a saturated solution of hydrochloric acid in the inactive-alcohol at 105° is an optically inactive colourless liquid, boiling at 98·9° under a pressure of 733·8. Its density at 0° is 0·8928. *Amyl bromide* prepared in a manner precisely similar to the chloride boils at 120·4° under a pressure of 745·2. Its density at 0° is 1·2358. *Amyl acetate* is a colourless, optically inactive liquid, prepared by distilling a mixture of acid amyl sulphate and dry sodium acetate. It boils at 138·6° under a pressure of 743·5, and its density at 0° is 0·8838. *Amyl valerate* obtained, together with some valeric aldehyde and traces of valeric acid, by Pierre and Puchot's method of oxidising the alcohol at a low temperature by means of chromic acid mixture, is optically inactive. It boils at 190·3° under a pressure of 748, and has a specific gravity of 0·870 at 0°. When decomposed by an alcoholic solution of potassium hydrate, it yields potassium valerate, from which the inactive *valeric acid* may be obtained by distilling it with dilute sulphuric acid. When dry it boils constantly at 174·1°, under a pressure of 723·5. The salts of this acid, having already been examined by Pedler and by Erlenmeyer and Hell, were not further investigated by the author, who hopes, however, to be able to continue the study of other derivatives of the inactive amyl alcohol.

C. E. G.

Preparation of Glycol (a Correction). By O. LIETZEN-MAYER (*Deut. Chem. Ges. Ber.*, ix, 1472).—The author could formerly not obtain glycol by Demole's method, but by following strictly the instructions of the latter, he has now succeeded.

C. S.

Reduction of Levulose. By H. D. KRUSEMANN (*Deut. Chem. Ges. Ber.*, ix, 1465—1469).—Pure levulose was obtained by heating inulin with water under pressure, and its aqueous solution treated

with sodium amalgam in the cold; at the same time an equal quantity of pure dextrose was subjected to the same treatment. Both yielded, as chief product, *mannite*, a small quantity of Bouchardat's alcohols being also formed. C. S.

Optical Properties of Mannite. By A. MUNTZ and E. AUBIN (*Compt. rend.*, lxxxiii, 1213).—Vignon has shown that borax develops a dextrogyratory power in mannite. The authors find that metallic salts in general, and particularly the salts of the alkalis and alkaline earths, develop a similar power. Alkalis, on the contrary, develop a levogyratory power. The action is not permanent, for when the salt is removed, the mannite again becomes inactive, and if the alkali be saturated by an acid, the levogyratory power becomes dextrogyratory.

Mannite from various sources was examined, but in no case was any sensible difference observed in its action upon light.

The various mannites in solution gave a mean deviation of -0.12 ; with borax, $+22.34$; with caustic soda, -3.4 . The corresponding nitromannites gave a mean deviation of $+12.4$. C. W. W.

Optical Properties of Starch. By WALTER BAILY (*Phil. Mag.* [5], ii, 123—126).—The appearance of a grain of starch under the microscope is pretty generally known: it exhibits a spot surrounded by a series of faint lines forming closed curves. The spot can be shown to be internal, and the lines to be produced by the foreshortening of a series of transparent envelopes.

Under the polariscope, the grain appears to be marked with a black or white cross according as the Nicol's prisms are parallel or at right angles to each other; it is evident therefore that the light which emerges from the starch at points on the cross, is plane-polarised in the plane of polarisation of the lower Nicol, while the light from points in the spaces is elliptically polarised, the polarisation being most nearly circular at points most distant from the cross, since the revolution of the upper Nicol occasions there the least change in the illumination.

The optical properties of these grains is explained by the author as follows. Taking the case of a circular disc, he supposes that the substance is doubly refracting, with two axes of elasticity at each point in the plane of the disc, one of them being directed towards the centre of the disc. The arrangement of the axes of elasticity in the disc is therefore given by a family of lines radiating from the centre, and a family of circles described about it. Plane-polarised light passing through such a disc will emerge without change along the diameters which lie parallel and perpendicular to the plane of polarisation: for the vibration will coincide with one of the axes of elasticity at every point on these diameters; but at other points the light will be resolved into a vibration parallel to each axis, and as these two vibrations will be unequally retarded, the light will become elliptically polarised, and the change will be greatest in the middle of the quadrants, where the axes are equally inclined to the plane of polarisation.

In an oval starch grain seen sideways, the foreshortened parts of the ends will give a series of ovals, whose optical effects will be

similar to those of an oval disc. Assuming that the coats are doubly refracting, and that one axis of elasticity at each point is normal to the coat, and differs in value from the other two which lie in the tangent plane to the coat, then, in each coat at points where it is not foreshortened, the normal axis will be more or less in the direction of the ray, and the effect of the coat on the light will be little or none, since the tangential axes are nearly, if not quite, equal; but where the coat is most foreshortened the normal axis will be at right angles to the ray, and the effect of the coat on the light will be greatest. Hence the effect of the whole grain on the light will be nearly the same as that of a section taking in the nucleus and those parts of the coats which are most foreshortened. We may therefore conclude that a grain of starch really consists of a series of coats round a nucleus, each coat being doubly refracting, and having one axis of elasticity normal and two tangential, and that the normal axis differs more from the others than they differ from one another. J. W.

Chlorinated Acetals and some Derivatives. By O. KREY (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 84—91).—The author finds that the chlorinated derivatives of acetal (mono-, di-, and tri-chlor-acetal) are obtained in largest quantity by treating a mixture of 2 parts of absolute alcohol and 2 parts of water with 3 parts sulphuric acid and 3 parts of manganese dioxide, distilling off two-thirds of the liquid, and treating the cooled distillate with chlorine till it begins to be turbid. Monochlor- and dichloracetal are colourless liquids of agreeable odour, boiling at 154—159° and 180° respectively, as stated by Paternò. Trichloracetal crystallises in large white needles, which melt at 83° and begin to decompose at 190°.

Dichloracetal and Phosphorus Pentachloride.—These bodies act upon each other in the manner indicated by the equation—

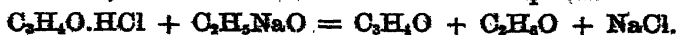


The first of these products is analogous to the compound of aldehyde and ethyl chloride which Wurtz and Frappoli obtained by the action of hydrogen chloride on aldehyde and alcohol. It is intermediate between dichloracetal and the compound $\text{C}_2\text{H}_5\text{Cl}$, which Paternò obtained by the action of phosphorus pentachloride on dichloraldehyde.

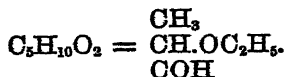
J. R.

Reactions of Acrolein Hydrochloride. By A. TAUBERT (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 1—25).—1. *With Alcoholic Sodium Ethylate.*—When acrolein hydrochloride is warmed with a slight excess of sodium ethylate formed by dissolving 1 part of sodium in 9 parts of absolute alcohol, a violent reaction takes place; sodium chloride is separated in large quantity; and a liquid is formed, from which, by distillation with water and other processes, the following bodies have been obtained, together with some others not yet investigated.

a. *Metacrolein*, formed in accordance with the equation:



b. A body formed by the replacement of chlorine in acrolein hydrochloride by ethoxyl, and hence having the formula—



This is a colourless oily liquid, of peculiar aromatic odour, and bitter acrid taste, burning with a blue non-luminous flame. It dissolves in alcohol, ether, and water. Sp. gr. 0.936 at 4°. It begins to boil at 130°, but cannot be distilled without decomposition.

c. A thick oily liquid, of yellow colour and neutral reaction, dissolving easily in alcohol and ether, but not in water, and giving, on analysis, numbers agreeing with the formula $\text{C}_6\text{H}_8\text{O}_2$. This substance is decomposed by distillation, yielding at first a large quantity of acrolein, and afterwards the compound $\text{C}_5\text{H}_{10}\text{O}_2$ (b) perfectly pure, whilst a black carbonised mass is left in the retort.

d. A resinous substance having the composition and properties of *hexacrylic acid*, $\text{C}_{18}\text{H}_{24}\text{O}_6$.

e. A body which agrees approximately with the formula, $\text{C}_9\text{H}_{13}\text{NaO}_4$, and may, therefore, be regarded as the sodium salt of a monobasic acid, $\text{C}_9\text{H}_{14}\text{O}_4$ (*triacrylic acid*), formed by the combination of 3 mols. of acrolein with 1 mol. of water.

2. *With Phosphorus Oxychloride and Trichloride*.—Acrolein hydrochloride is not attacked by phosphorus oxychloride in the cold, but when it is warmed therewith, a brisk reaction takes place, hydrogen chloride is evolved in large quantity, and the compound is carbonised, and in the end completely decomposed.

Phosphorus trichloride does not act upon acrolein hydrochloride, even when boiled with it.

3. Acrolein hydrochloride reacts with *absolute alcohol* at 100°, with *potassium hydrate* at 140°, and with *potassium acetate* at 180°, but none of the products of these reactions have as yet been isolated.

A. Genther, in some remarks on the foregoing paper, suggests that the substance c may be an *alcohol-metacrolein*, analogous to metacrolein, formed thus:

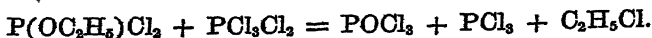


This formula, it is true, accords less nearly with the author's analytical results, but it is more consistent with the mode of formation of the body, and with its behaviour when heated. J. R.

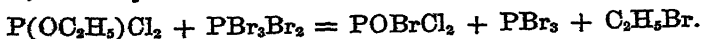
Polybasic Compounds of the Acids of Nitrogen. By F. MEISSNER (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 26—44).—The author has attempted to obtain polybasic ethyl-compounds of trivalent and quinquivalent nitrogen, by the action of ethyl iodide on basic lead nitrates and nitrites, but without success, the ethyl-radicle being in all cases eliminated in the form of ethyl-ether. J. R.

Decompositions of Phosphorus-compounds. By A. GENTHER (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 104—116).—1. *Phosphorus*

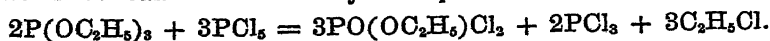
Oxethylchloride and Phosphorus Pentachloride.—These substances do not act upon each other at the ordinary temperature, but when they are heated together in the water-bath, the following reaction takes place:



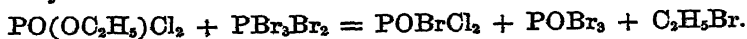
2. *Phosphorus Oxethylchloride and Phosphorus Pentabromide*, when heated together, yield phosphorus oxybromochloride, phosphorus tribromide, and ethyl bromide:



3. *Ethyl Phosphite and Phosphorus Pentachloride* react upon each other in the manner indicated by the equation—



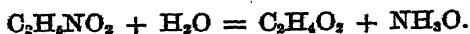
4. *Phosphorus Oxethyloxychloride and Phosphorus Pentabromide* react to form phosphorus oxybromochloride, phosphorus oxybromide, and ethyl bromide:—



The foregoing reactions all reveal the important fact that phosphorus pentachloride and pentabromide, in their action on the oxethyl-compounds of trivalent phosphorus, behave like mixtures of trichloride and free chlorine, and of tribromide and free bromine, respectively.

J. R.

Action of Various Bodies on Nitroethane. By H. WEENER (*Jenaische Zeitschr. f. Naturwissenschaft*, x, 70—83).—The author has examined the action of several substances on nitroethane, with the view of obtaining evidence bearing upon the constitution of that body. The only definite result arrived at is that nitroethane is resolved by the action of dilute acids (phosphorous, sulphuric, hydrochloric, sulphurous) into acetic acid and hydroxylamine, in accordance with the equation—



J. R.

Action of Chlorine on Acetonitril. By H. BACKUNTS (*Deut. Chem. Ges. Ber.*, ix, 1594).—Chlorine alone does not act on acetonitril, and but slowly in presence of iodine, with formation of trichloracetoneitril.

C. S.

Action of Alkalis on the Chlorinated Acetonitrils. By H. BACKUNTS and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1591).—When monochloracetoneitril is boiled with milk of lime, it is converted into glycollic acid; dichloracetoneitril yields, under the same conditions, dichloroacetic acid, while trichloracetoneitril is resolved into carbon dioxide and chloroform. Potash acts in a similar way.

C. S.

α -Monochloropropionitril. By H. BACKUNTS and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1592—1593).—To prepare this compound

ethyl α -monochloropropionate is shaken with concentrated ammonia until it is dissolved; on evaporation the corresponding amide is left behind, which crystallises from water or alcohol in glistening scales, melting at 80° . On heating it with phosphorus pentoxide, the nitril is obtained as a liquid having an irritating smell, and boiling at 121 — 122° . Ammonia converts it again into the amide, and a mixture of alcohol and hydrochloric or sulphuric acid into chloropropionic ether, while on boiling it with milk of lime, lactic acid is formed. C. S.

Constitution of Dichloropropionitril. By H. BACKUNTS and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1593—1594).—When propionitril is treated with chlorine, only two atoms of hydrogen are replaced, even in presence of iodine or molybdc chloride. The product is a liquid boiling at 103 — 107° . By acting on it with sulphuric or hydrochloric acid and alcohol, it yields an ethyl dichloropropionate identical with that obtained by Klimenko from the chloride, which he prepared by the action of phosphorus pentachloride on pyruvic acid; from this it follows that the nitril has the constitution $\text{CH}_3\text{CCl}_2\text{CN}$. By the action of ammonia on the ether the amide is obtained, melting at 115 — 116° , and yielding with phosphorus pentoxide the pure nitril which boils at 105° ; concentrated hydrochloric acid converts it into dichloropropionic acid, which is a liquid boiling at 190 — 195° , and smelling like the volatile fatty acids. It is soluble in water and alcohol, but aet in strong hydrochloric acid. C. S.

On the Ferrocyanides of Wyruboff. By A. ATTERBERG (*Deut. Chem. Ges. Ber.*, ix, 1475—1477).—Wyruboff has published in the last number of *Ann. Chim. Phys.* a research on these compounds, in which he doubts some of the results of the author's investigation on the same subject. In reply it is now shown, that Wyruboff's methods of analysis are faulty and most of his formulæ and equations full of mistakes. C. S.

Behaviour of Melam to Sulphuric Acid. By J. H. JÄGER (*Deut. Chem. Ges. Ber.*, ix, 1554—1557).—Liebig, Knapp, and other chemists having obtained different results from the action of sulphuric acid on melam, it occurred to the author that this might be due to the temperature at which the reaction took place.

When six parts of pure concentrated sulphuric acid are added to one part of dry, finely-powdered melam, the temperature rises to 120° , but immediately sinks again. If the flask is placed on a water-bath, the melam dissolves perfectly, but the temperature never exceeds 100° . After the lapse of half an hour the liquid is filtered through asbestos and precipitated by alcohol. The precipitate is bulky, of a dirty-white colour, and insoluble in cold water, though it is almost entirely dissolved by hot water. The hot solution deposits on cooling a mass of fine needle-like crystals of melamine sulphate $(\text{C}_3\text{H}_6\text{N}_6)_2\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. From this salt the melamine is thrown down by caustic soda or an alkaline carbonate, and is purified by recrystallisation. The part of the original precipitate which is insoluble in hot water is probably ammelime. Perhaps a part of the first-formed melamine is

converted into ammeline by the further action of the sulphuric acid, with evolution of ammonia and addition of the elements of water. Neither Liebig's nor Gerhardt's ammelide is formed by the action of sulphuric acid on melam at 100° ; at higher temperatures the author obtained only that of Gerhardt.

If the mixture of sulphuric acid and melam is heated to 150° a lively reaction takes place, the mass froths up, and the temperature quickly rises to 210° . The precipitate obtained in this case by alcohol consists of Gerhardt's ammelide. If the nitrite of this body or the free substance is dissolved in hot ammonia, fine acicular crystals are formed, which, however, undergo decomposition so readily that their composition has not been determined. Gerhardt and Gabriel obtained only ammelide from melam and sulphuric acid at a higher temperature. The author has not been able to prepare Liebig's ammelide in any way. The melamine treated with sulphuric acid at 150° yields only ammelide. According to Liebig, ammelide, $C_6N_6H_8O_8$, should be formed from ammeline nitrate, but the author could obtain only a body which forms well-crystallised salts with acids.

G. T. A.

Structure of Cyanic Acid. By A. FLEISCHER (*Deut. Chem. Ges. Ber.*, ix, 1459—1461).—A reply to Nencki and Claus. C.S.

Constitution of Guanamine and Cyanuric Acid. By M. NENCKI (*Deut. Chem. Ges. Ber.*, ix, 1552—1554).—This paper is a reply to some comments of Claus on a previous article of the author (*Berichte*, ix, 1008), and maintains the carbimide nature of cyanuric acid.

G. T. A.

Glyoxaline. By G. WYSS (*Deut. Chem. Ges. Ber.*, ix, 1543—1545).—By acting with ammonia on glyoxal, Debus obtained two bases, glycosine, $C_6H_8N_4$, and glyoxaline, $C_3H_4N_2$, the latter being the chief product of the reaction. The author is engaged in investigating this latter body. The aqueous solution of glyoxaline leaves on evaporation a syrup, which was submitted to fractional distillation. At first a brown liquid with a somewhat unpleasant smell passed over, but above 250° the distillate solidified immediately to a fine mass of white crystals. A second rectification leaves the base pure. Glyoxaline forms thick prisms of mother-of-pearl brilliancy, which are strongly alkaline, and when warm have a faint fish-like smell, but are inodorous when cold. It is easily soluble in water, alcohol, and ether, but is not deliquescent when pure. It melts at $88-89^{\circ}$ and boils at 255° (uncorrected). The vapour-density of the free base was found to be 2.26 (air = 1). The author is endeavouring to arrive at the constitution of glyoxaline, and will also further examine glycosine if he can succeed in preparing it in larger quantities.

G. T. A.

Results of an Exhaustive Chlorination of Aromatic Substances. By G. RUOFF (*Deut. Chem. Ges. Ber.*, ix, 1483—1500).—The substances which were examined were first treated with chlo-

rine at the common temperature, then at a higher temperature, and the reaction was finished by heating in sealed tubes with iodine chloride from 100—350°; in some cases antimony pentachloride was also used.

Diphenylmethane, anthracene, phenanthrene, tribenzylamine, anisol, and cresol gave hexchlorobenzene and tetrachloromethane.

Diphenyltrichlorethane and phenetol yielded hexchlorobenzene and hexchlorethane.

Naphthalene, cymene, oil of turpentine, camphor, thymol, and phenol were converted into a mixture of hexchlorobenzene, hexchloroethane, and tetrachloromethane, while azobenzene, diphenylamine, resorcin, and chloranil gave only hexchlorobenzene and pyrogallol, a mixture of tetrachloromethane and hexchlorethane, but no hexchlorobenzene.

Triphenylamine yields, as chief product, perchlorotriphenylamine, $(C_6Cl_5)_3N$, crystallising from a hot mixture of benzene and alcohol in short white needles, which do not melt at 270°. At the same time some hexchlorobenzene was formed.

Diphenyl is converted into perchlorodiphenyl, $C_{12}Cl_{10}$, crystallising from hot benzene in glistening grains, which do not melt at 270°, and sublime when strongly heated. This compound is not changed by heating it with antimonie chloride to 350°, or by passing its vapour with chlorine through a red-hot tube.

The author has also examined the properties of perchloronaphthalene, which Berthelot and Jungfleisch had not obtained quite pure. It dissolves sparingly in alcohol and glacial acetic acid, more freely in benzene, petroleum-naphtha and chloroform, and crystallises in long, pale-yellow, glistening, brittle needles, melting at 203°. C. S.

The Exhaustive Action of Bromine on some Aromatic Bodies.
By E. GESSNER (*Deut. Chem. Ges. Ber.*, ix, 1505—1512).—*Benzene*, C_6H_6 .—The highest bromine substitution-product yet prepared of benzene is the pentabrombenzene, which Kekulé obtained by heating nitrobenzene with bromine. Bromine containing iodine in solution was allowed to drop into cooled benzene; a powerful evolution of hydrobromic acid took place, and after a short time a crystalline mass was formed. This mass, consisting probably of tri- and bi-brombenzene, was fused with excess of benzene, and heated at from 80° to 100°, till on opening the tube only a little hydrobromic acid escaped. After about thirty hours' heating at nearly 400°, a mass of long prismatic needles was found in the tube. After washing with soda, recrystallisation from toluene, and sublimation, *perbromobenzene*, C_6Br_6 , was obtained in the pure state. In properties it is very similar to perchlorobenzene, but it melts at a much higher point, viz., over 310°. It sustains a red-heat without alteration, air being excluded. It is moderately soluble in boiling benzene and toluene, easily in boiling aniline and turpentine, with more difficulty in boiling petroleum-spirit, glacial acetic acid, and chloroform, and crystallises in every case in beautiful white needles. It is insoluble in alcohol and ether.

Toluene, $C_6H_5-CH_3$.—Beilstein and Kühlberg obtained perchlorobenzene by the action of antimony pentachloride on toluene at high temperatures. The bi-brominated toluene has so far been obtained as the highest product. The toluene was treated just as the benzene was previously. The results were analogous to those obtained by the chlorination of toluene:



Perbromobenzene, C_6Br_5 , thus obtained possessed all the properties characterising this body directly derived from benzene.

Azo-benzene, $(C_6H_5)_2N_2$.—Azobenzene was treated with bromine in presence of iodine, and heated gradually to about 350° . Forty-five hours were required for the complete bromination, no more hydrobromic acid being then given off. Nitrogen was given off, and perbromobenzene formed:



Phenol, $C_6H_5.OH$.—Perchlor- and perbromophenol are known. The action of bromine in presence of iodine was now tried at tolerably high temperatures (over 220°). The temperature was gradually raised. The experiment was conducted in a sealed tube. Perbromobenzene was obtained and oxygen set free. This, however, immediately combined with carbon, and so escaped as carbon dioxide.

Naphthalene, $C_{10}H_8$.—Perchloronaphthalene is known, but up to this time the highest bromine substitution-product was pentabromonaphthalene, obtained by heating dibromonaphthalene with bromine to 150° . A quantity of dibromonaphthalene was now heated in closed tubes with bromine and iodine to 100° ; afterwards the temperature was raised to 150° and finally to 350° . Long needle-shaped crystals were finally obtained on recrystallising from chloroform. This product turned out to be, not perbromonaphthalene, but hexbromonaphthalene, $C_{10}H_2Br_6$.

Hexbromonaphthalene, $C_{10}H_2Br_6$, resembles closely in appearance and properties perchlorobenzene, crystallising in delicate needles, and dissolving in hot benzene, toluene, chloroform, and aniline; but not in alcohol and ether.

Diphenylamine, $(C_6H_5)_2NH$.—Diphenylamine was treated in the cold with bromine. The action was very powerful, streams of hydrobromic acid escaping. When the action became exhausted, the fluid mass, with addition of iodine, was heated in sealed tubes to 100° for many hours, and then slowly and gradually to 350° . The final product was treated with warm sodium-hydrate solution, and then twice recrystallised from chloroform. In this manner delicate white needles were obtained consisting of—

Decarbomodiphenylamine, $C_{12}HBr_{10}N$, probably $(C_6H_5)_2NH$. This body melts above 310° , and dissolves but slightly in boiling benzene, toluene, and chloroform. In alcohol and ether it is quite insoluble.

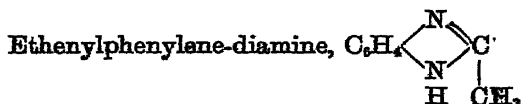
The prismatic crystals obtained in the sealed tubes at 250° were next examined and proved to be

Octobromodiphenylamine, $C_{12}H_3Br_9N$. Melting point = $302-305^\circ$. More soluble in benzene, toluene, and chloroform than the previous derivative, and crystallising from these solutions in small colourless prisms. W. S.

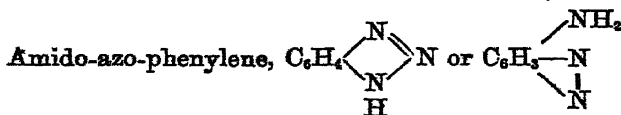
Condensations in the Ortho-Group. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, ix, 1524—1530).—The author has observed, in a number of researches lately made, that the changes taking place in the aromatic ortho-group, are in many cases different from those which occur in the other two groups, the removal of certain atoms sometimes leading to internal condensations, for which we find no analogy in the meta- and para-groups. Researches were resolved upon to determine experimentally the nature of the differences in the behaviour of analogous bodies of the ortho-group, and those of the other groups. The following are the results of observations already made, the main bulk of the labour of systematic research in this direction having yet to follow:—

Such internal condensations as were referred to above, were observed in the study of the *ortho-diamines* and their behaviour with acetic acid and with nitrous acid.

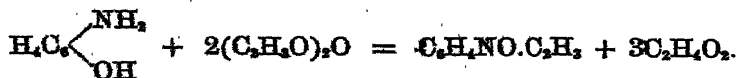
By the action of *acetic acid*, orthophenylenediamine yielded—




and by the action of nitrous acid it yielded—



1. *Ortho-amidophenol and Acetic Acid.*—Ortho-amidophenol and acetic anhydride, heated together for a long time in a retort with reversed condenser, and then distilled, yielded acetic acid, unaltered anhydride, and a fluid boiling at above 200° . By treatment with potash till alkaline, drying over potassium carbonate, and rectifying, a colourless liquid, boiling at 200° to 201° , is obtained. It has a very peculiar odour, like that of acetamide, is insoluble in water, easily soluble in alcohol, and yields a compound with calcium chloride. Analysis and vapour-density determination lead to the formula, C_6H_7NO . The reaction is as follows:—



The constitution of the body appears to be, C_6H_4  and it

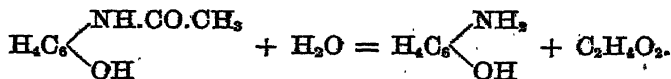
is therefore *ethenyl-amidophenol*. Its spec. grav., at 0° is 1.1365. It soon becomes red on exposure to the air. On leaving it for a long time in contact with water, a crystalline compound separates out, formed by taking up the elements of water: this is *acetamidophenol*.

Ethenyl-amidophenol is a base; it is easily soluble in dilute hydrochloric and sulphuric acids, but its salts are difficult to obtain, because they are so easily decomposed in presence of water. The sulphate was only once obtained, as an extremely soluble body, the aqueous solution of which, on treatment with ammonia, yielded the base as an oil. If the sulphuric acid solution be slightly warmed, acetyl-amidophenol is formed, instead of the sulphate. The chloride is more stable than the sulphate. The chloride of ethenyl-amidophenol is obtained crystallised under the air-pump, and then dissolves again in water, without alteration. By addition of platinum chloride to the hydrochloric acid solution, a yellow, crystalline precipitate is obtained of the platinum double salt, $(C_6H_7NOHCl)_2.PtCl_4$. This double salt is very soluble in *dilute* alcohol, but splits up at the same time into its component parts.

Acetyl-amidophenol, $H_4C_6 \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ N \\ \diagdown \quad \diagup \\ H \end{array} C_2H_3O$. Easily obtained by warm-

ing the sulphuric acid solution of *ethenyl-amidophenol* on the water-bath. Right angled, four-sided plates soon separate out, and the crystalline mass needs only one re-crystallisation from dilute alcohol, to furnish the product quite pure. This body is easily soluble in hot water and alcohol, and also in potash; melts at 201°, and distils without decomposition, at least in small quantities. Distilled with phosphoric anhydride, it yields ethenyl-amidophenol.

By heating it with concentrated hydrochloric acid in sealed tubes to 130°, a solution is obtained, from which amidophenol is separated by means of sodium carbonate. The following decomposition takes place:—



Similarly also ethenyl-amidophenol splits up when heated with alcoholic potash to 120°. Everything was dissolved, and after dilution with water, the amidophenol was precipitated by carbon dioxide.

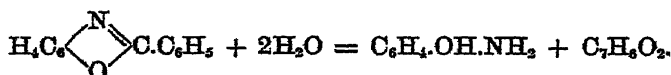
2. *Amidophenol and Benzoic Acid*.—Benzoyl chloride and amidophenol react upon each other when gently warmed, with liberation of hydrochloric acid. This reaction being complete, the mixture is distilled, and the portion which boils between 314° and 317° and soon solidifies, is separated. This is almost pure benzenyl-amidophenol. The fraction boiling lower, viz., between 290° and 312°, can also be treated so as to extract still more of the body. For this purpose it is warmed with soda-solution, to extract benzoic acid, and the residue is repeatedly crystallised from dilute alcohol.

Benzenyl-amidophenol, $C_6H_5 \begin{array}{c} O \\ \diagup \quad \diagdown \\ N \end{array} C_6H_5$, crystallises in splendid,

colourless, shining laminæ, melting at 103° , and becoming, on long exposure to the air, of a reddish colour. It is not soluble in water, but in alcohol is easily so. These properties agree with those of a body obtained by Morse, from amido-phenol hydrochloride and benzoyl chloride. Morse gives it the formula, $C_6H_4(OH)NH.CO.C_6H_5$, and terms it benzoyl-amidophenol. The author doubts the correctness of Morse's deductions.

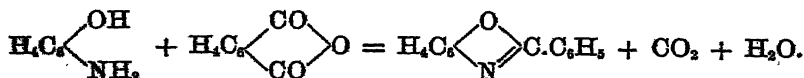
Benzenyl-amidophenol dissolves in dilute sulphuric acid, and the solution can be boiled without alteration. When heated to 120° in a sealed tube, with sulphuric acid, this body is dissolved, probably as sulphate, but can be precipitated unaltered by much water. Benzenyl-amidophenol is a very weak base, and its salts are very easily decomposed. It dissolves in concentrated hydrochloric acid, but is left behind on evaporation of the acid, as benzenyl-amidophenol. A platinum double salt is obtained by treating the hydrochloric acid solution of the body with platinum chloride. The precipitate is decomposed by water, but may be crystallised from alcohol by addition of hydrochloric acid, in beautiful yellow prisms, the formula of which is $(C_{12}H_9NOHCl)_2PtCl_4$.

By heating with concentrated hydrochloric acid to 130° , in a sealed tube, benzenyl-amidophenol is decomposed into amidophenol and benzoic acid, according to the equation—

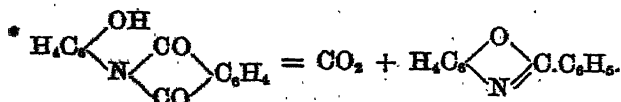


The intermediate product expected viz., benzoyl-amidophenol, was not obtained.

3. *Amidophenol and Phthalic Acid*.—A mixture of phthalic anhydride and amidophenol was submitted to dry distillation, when after some time decomposition took place. Much gas escaped, and a small quantity of a body distilled over, which soon crystallised. This was warmed with soda, to remove phthalic acid, and then crystallised from alcohol. Its melting point was then 103° , and it consisted of shining plates, and was actually benzenyl-amidophenol—



This research and the facts following show that benzenyl-amidophenol may be considered as a condensation-product of phthalamidophenol or oxyphthalanil—

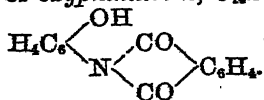


Phthalyl-amidophenol.

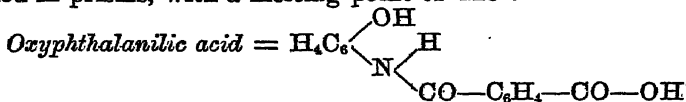
Benzenyl-amidophenol.

That the formation of phthalyl-amidophenol precedes that of benzenyl-amidophenol was proved as follows:—Phthalic anhydride and

amido-phenol in molecular proportions are heated in a retort together, at about 220°. The solid mass is then pulverised and extracted with dilute alcohol, whereby crystals are obtained, melting at 220°. They are soluble in alcohol and toluene, and have the composition of *oxyphenyl-phthalimide*, or *oxyphthalanil*, $C_{14}H_9NO_3$, or



This compound is soluble in cold solutions of alkaline hydrate; in alkaline carbonate solutions on warming. If the sodium carbonate solution of the body be evaporated to dryness, and the residue taken up with absolute alcohol in the cold, and the alkaline solution be evaporated, a syrup remains, which on standing, after addition of a little water, deposits beautiful needles. This body was found to be sodium *oxyphthalanilate*, $C_{14}H_9NaNO_4$. By decomposing with hydrochloric acid, and recrystallising the precipitate which arises, from alcohol, the acid is obtained in prisms, with a melting point of 223°.



The formation of ethenyl- and benzenyl-amidophenol is characteristic of the ortho-compound, as the author has not succeeded in preparing any corresponding derivatives from paramidophenol. When paramidophenol is treated with acetic anhydride, just as ortho-amido-phenol was, till all the acetic anhydride is distilled off, a decomposition sets in, whereby almost the whole mass is carbonised. But if the distillation be stopped, after heating to 160°, and the residue be re-crystallised from hot water, with addition of animal charcoal, white crystals are obtained, melting at 150°—151°, and having the formula, $C_{10}H_{11}NO_3$,

which is that of *diacetyl-amidophenol*, $\text{H}_4\text{C}_6 \begin{array}{c} \text{O.C}_2\text{H}_5\text{O} \\ \diagup \\ \text{N} \text{---} \text{H} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_5\text{O} \end{array}$. By the action

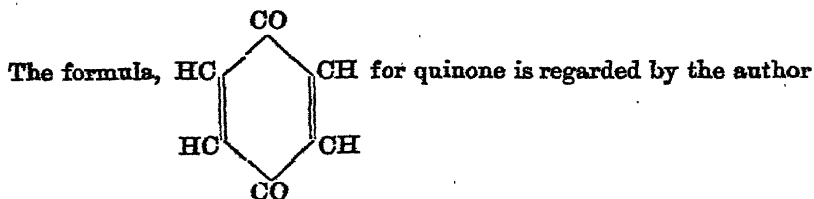
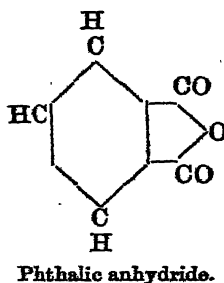
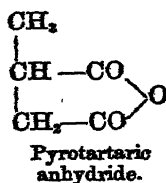
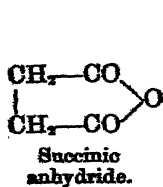
of benzoyl chloride on paramidophenol also, *dibenzoyl-amidophenol*, $\text{H}_4\text{C}_6 \begin{array}{c} \text{O.C}_7\text{H}_5\text{O} \\ \diagup \\ \text{N} \text{---} \text{H} \\ \diagdown \quad \diagup \\ \text{C}_7\text{H}_5\text{O} \end{array}$ is obtained. It is a body soluble with difficulty, and melting at 231°.

The author, though so far having only worked with nitrogen-compounds, believes these reactions to be of universal significance. Other chemists have already observed similar condensations, evidently realisable only in the ortho-group, e.g., the formation of coumarin (Perkin), and of piperonal (Fittig). The derivatives of phthalic acid (Baeyer), the formation of phthalein, and the recently discovered syntheses of anthraquinone and its derivatives, all stand in direct connection with the ortho-position of the carboxyl-group in phthalic acid. It appeared important to determine in the next place whether other ortho-compounds would yield reactions similar to those furnished by the phenols.

This was found to be the case, bodies being obtained from salicylic acid with properties similar to those which Baeyer ascribes to the phthaleins. The formation of rosolic acid from salicylic aldehyde (Liebermann) is also an example of the case in point. From salicylic acid and resorcin by abstraction of water a beautiful yellow dye, with fine green fluorescence was obtained. By brominating this, a red colour was obtained, communicating a beautiful tint to silk. The theoretical considerations deducible from these results are being worked out.

Looking at Kekulé's benzene-chain, it will be observed that the substituted groups in the ortho-compounds, stand in the positions of neighbouring carbon atoms. In this light Gräbe assumed, in the case of such bodies, an internal "binding together," or condensation. Thus he adopted the view of the ortho-position of quinone and naphthalene.

According to this view a close analogy is observable between succinic anhydride or pyrotartaric anhydride, and phthalic anhydride—



as improbable.

W. S.

Preparation of Benzene- and Paratoluene Sulphydrates.

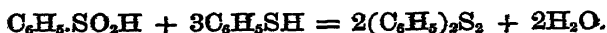
By R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1587—1588).—These compounds are readily obtained by adding the zinc or sodium-salts of the corresponding sulphinic acids in small quantities to a mixture of hydrochloric acid and zinc, which must be kept cold.

C. S.

Formation of Benzene- and Paratoluene Disulphide. By

R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1588—1591).—When sulphonic and sulphinic acids are treated with nascent hydrogen, they generally yield, besides a sulphydrate, also some disulphide, the quantity of which increases when the mixture is not kept cold. The formation of the disulphide is due to the action of the sulphinic

acid on the sulphhydrate, for on heating 1 mol. of benzenesulphinic acid with 3 mol. of the sulphhydrate to 100°, the following reaction takes place:—



C. S.

Iodo- and Bromazo-compounds of Benzene. By S. GABRIEL (*Deut. Chem. Ges. Ber.*, ix, 1405—1411).—On heating a mixture of 13 parts of metabromonitrobenzene, 8 of caustic potash, and 50 of alcohol, *azoxydibromobenzene*, $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2\text{O}_2$, is formed, crystallising from hot acetic acid in pale yellow, broad prisms, melting at 111—111·5°; in sulphuric acid it dissolves with a yellow colour, which on heating changes into a blood-red. By the action of hot ammonium sulphide it is converted into *hydrazodibromobenzene*, $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{N}_2$, crystallising from hot dilute alcohol in short, thick, white, or reddish prisms, melting at 107—109°. Ferric chloride oxidises it to *azodibromobenzene*, $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2$, crystallising in flat needles, melting at 125·5°. The same compound is formed by boiling an alcoholic solution of the hydrazo-compound for some time with animal charcoal. On boiling the hydrazo-compound with hydrochloric acid, the isomeric *dibromobenzidine*, $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{N}_2$, is obtained, forming small, glistening crystals, melting at 151·5—152°, and forming crystalline salts.

When a mixture of 10 parts of *pariido-nitrobenzene*, 16 of potash, and 100 of alcohol is boiled, *azoxydi-iodobenzene* is obtained, crystallising in yellow plates, melting at 199—199·5°. On heating it with alcoholic ammonium sulphide in a sealed tube to 100°, *hydrazodi-iodobenzene* is formed, crystallising in white or yellowish needles or plates, melting above 100°, and decomposing at the same time. By adding ferric chloride to its alcoholic solution, or boiling it with animal charcoal, *azodi-iodobenzene* is obtained in reddish scales, melting at 237°; the same compound is formed by the action of hot sulphuric acid, and separates on cooling from the blood-red solution in brown needles, having a steel-blue lustre while in the liquid.

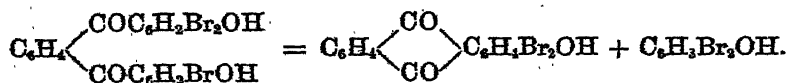
On boiling 10 parts of *meta-iodonitrobenzene* with 8 of alcohol, and 50 of alcohol, an *azoxydi-iodobenzene* is formed, crystallising in flat, compact, pale yellow needles. Its hydro-compound forms colourless or yellowish crystals, melting at 89—90°, and the azo-compound crystallises in orange-red needles, melting at 150°. C. S.

On the Phthalin and Phthalidein of Phenol. By A. BANYER (*Deut. Chem. Ges. Ber.*, ix, 1230—1239).—I. **PHTHALIN GROUP.**—*Phenol-phthalin.*—The preparation of this body has been previously described by the author. It forms pointed crystals of the triclinic system. Nitric acid acts upon it in the cold to form a product which is converted by tin and hydrochloric acid into *amidophthalin*. The hydrochloride of this base forms colourless crystals, which dissolve with blue colour in soda-ley, and give with sulphuric acid at 170° an anthraquinone derivative, apparently alizarin.

Tetrabromophthalin, $\text{C}_{20}\text{H}_{10}\text{Br}_4\text{O}_4$, is formed by the action of bromine

in excess on phthalein. It crystallises in short colourless prisms, which melt at 220—230°, and are sparingly soluble in alcohol and glacial acetic acid. In alkalis it dissolves with violet colour, which disappears with excess of the solvent; but the violet ammoniacal solution is not so decolorised.

Dibromozanthraquinone, $C_{14}H_6Br_2O_2$.—This body is formed, together with dibromophenol, when tetrabromophthalein is heated to 150° with 20 times its weight of strong sulphuric acid—



It is thrown down by water from the sulphuric solution as a grey precipitate, which crystallises from alcohol in reddish-yellow needles. It melts at 207—208°, and dissolves sparingly in alcohol, forming a coloured solution free from fluorescence. The *acetyl-compound* crystallises in golden-yellow needles, melting at 189—190°, and subliming without decomposition.

When dibromanthraquinone is heated to 200° with sodium hydrate for a few hours, and the fused mass is dissolved in water and acidified, a brownish precipitate is thrown down, which, when heated with acetic anhydride, yields yellow needles identical with the *acetyl-compound* of alizarin.

The dibromophenol formed in the above reaction sublimes at the ordinary temperature in thin laminae melting at 55—56°.

Phthalein Hydrate.—Phthalein, when fused with sodium hydrate, yields phthalin, which is not decomposed even when strongly heated; but when phthalein is heated to 190° with three times its weight of potassium hydrate for 24 hours, a substance is formed which crystallises from water in long needles agreeing in composition with the formula $C_{20}H_{14}O_4 + 2H_2O$.

Diacetyl-phthalein, $C_{20}H_{12}O_4(C_2H_3O)_2$, is readily formed by boiling phthalein with acetic anhydride. It crystallises from wood-spirit in colourless tables melting at 143°.

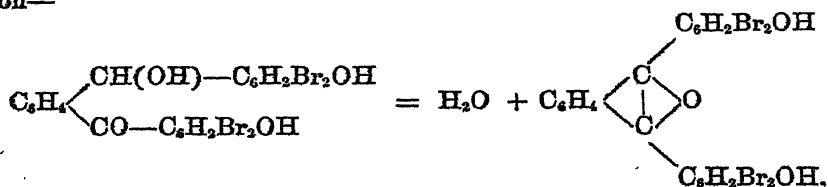
Phthalein chloride, $C_6H_4(COC_6H_4Cl)_2$, is formed by the action of phosphorus pentachloride at 125° on phthalein. It crystallises from glacial acetic acid and alcohol in beautiful silky laminae, which melt at 155—156°, and sublime without decomposition. It is reduced by hydriodic acid.

Phenol-phthalin, $C_{20}H_{14}O_4$, is formed by the action of zinc dust on phthalein dissolved in alcohol. It crystallises in small needles, and forms with potash a colourless solution which is coloured deep red by potassium ferricyanide, phthalein being reproduced. When boiled with acetic anhydride, it yields an *acetyl-compound*, which is difficult to purify.

Tetrabromophthalin.—This body may be obtained either by the reduction, by means of zinc, of tetrabromophthalein in ammoniacal solution, or by the action on phthalin of an excess of bromine in alcohol or glacial acetic acid. It crystallises readily, melts at 140°, and agrees in composition with the formula $C_{14}H_6Br_4O_4$. Alkalis dissolve it with-

out colour. Its *acetyl-compound* is crystalline, and melts at 165—166°.

II. PHTHALIDIN GROUP.—*Phenol-phthalidin*.—This substance is formed by the action of sulphuric acid on phthalin. It is thrown down by water from the sulphuric solution in the form of an amorphous yellowish precipitate, which dissolves readily in ether to form a yellow solution with greenish fluorescence. It is not crystallisable, and it oxidises easily in the air, so that it cannot well be analysed; but the composition of the bromine substitution-compound described below shows that its formula is $C_{20}H_{14}O_3$, and consequently that it is formed by the elimination of water from phthalin, into which substance it is reconverted by heating to 175° with water. It dissolves in alkalis without alteration in the absence of air. The formation and constitution of phthalidin may probably be expressed by the equation—



Tetrabromophthalidin, $C_{20}H_{10}Br_4O_3$, is thrown down by water from a solution of tetrabromophthalin in strong sulphuric acid, as a yellow precipitate, which crystallises from alcohol in yellow needles. It dissolves sparingly in alcohol and glacial acetic acid, freely in ether and acetone, and forms yellow solutions in alkalis.

Phenol-phthalidein.—This substance is obtained by the oxidation of phthalidin, the best reagent for the purpose being potassium manganate in alkaline solution. It crystallises from glacial acetic acid in colourless, thin, tabular crystals, and from weak spirit in thin laminae, which melt at 212°, and agree in composition with the formula $C_{20}H_{14}O_4$.

Phthalidein dissolves in potash-ley, with yellow colour, and is precipitated from the solution in colourless amorphous flocks by acids. It forms a deep violet solution with sulphuric acid, the smallest portion of phthalidein being enough to colour a large quantity of the acid. Its alkaline solution is reduced by zinc dust, phthalidin being re-formed.

Diacetyl-phthalidein, $C_{20}H_{12}O_4(C_2H_3O)_2$, is obtained by boiling phthalidein with acetic anhydride. It crystallises in small prisms melting at 109°.

Phthalidein chloride, $C_{20}H_{12}O_4Cl_2$, formed by the action of phosphorus pentachloride on phthalidein at 125°, crystallises from alcohol in silky needles, which melt at 156°.

Tetrabromophthalidein is formed either by the action of bromine on phthalidein, or by the oxidation of tetrabromophthalidin. It crystallises from alcohol in colourless opaque crystals, which melt above 280°. It dissolves in alkalis with yellow, and in strong sulphuric acid with blue colour. When heated to 140° with sulphuric acid, it behaves like tetrabromophthalein, yielding dibromoxanthraquinone. The *diacetyl*

compound, $C_{20}H_8Br_4O_4(C_2H_5O)_2$, formed by boiling it with acetic anhydride, melts at 182—183°.

Compounds of Phthalidein with Phenols.—When a phenol is added to the solution of phthalidein in strong sulphuric acid, the colour of the solution at once changes from violet to blood-red, and on addition of water a red amorphous precipitate is thrown down. The compound with phenol is an amorphous brick-red powder, which dissolves with intense violet colour in alkalis, and is thrown down again by acids as a yellowish-red precipitate. Its alcoholic solution, when treated with bromine, yields a crystalline substitution-product, soluble with blue colour in alkalis. Tetrabromophthalidein similarly combines with phenol, as does also phthalidein chloride. The phenol compound forms with ammonia at 150—160° a crystalline substance soluble in alkalis, and with blue colour in strong sulphuric acid.

The constitution of phthalidein is not yet determined. J. R.

Some New Phenol Colours. By C. REICHL (*Deut. Chem. Ges. Ber.*, ix, 1429).—On heating a mixture of two parts of glycerin, two parts of phenol, and three parts of sulphuric acid to 120—130°, a dark red mass results, dissolving in water with a brownish-yellow colour. Hydrochloric acid produces a precipitate, which after washing and drying, forms a dark brown powder, which could not be obtained in crystals. It is coloured red by alkalis, and gives lakes with baryta, alumina, and lead oxide. It dyes wool and silk, and yields, when heated with aniline, a red colour, which ammonia changes into reddish-violet. Colours are also formed by using pyrogallol or thymol in the place of phenol. C. S.

The Action of some Reagents on the principal Organic Colouring Matters. By G. SCURATI-MANZONI (*Gazzetta chimica italiana*, vi, 268—317).—The action of various reagents on colouring matters varies not only with the nature of the fibre and of the mordant employed, but also as to whether the colour is in solution or fixed on a fabric, so that the author has considered it necessary to examine the effect of various reagents, both on solutions and decoctions of the various organic colouring matters, and also on dyed swatches of wool and of cotton mordanted in various ways. The results of this laborious investigation are given in an extensive series of tables occupying 43 pages. C. E. G.

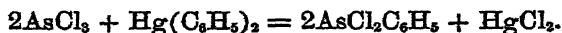
Aurantia. By R. GNEHM (*Deut. Chem. Ges. Ber.*, ix, 1245, 1429).—This dyestuff consisting of the ammonium salt of hexnitrodiphenylamine, produces splendid orange tints on wool and silk, but has the unpleasant property of producing blisters on the hands and arms of the workmen, and causing the fingers and arms to swell. The poisonous action is due to the substance itself and not to impurities.

Action of Silver Nitrite on Benzyl Iodide. By J. J. VAN BEMMEL (*Deut. Chem. Ges., Ber.*, ix, 1454).—Benzaldehyde, some benzoic acid, and nitric oxide are formed. C. S.

Action of Potassium Cyanide on the Isomeric Orthonitrometrabromobenzoic Acids. By J. J. VAN RENESSE (*Deut. Chem. Ges. Ber.*, ix, 1453).—Both are acted upon in an alcoholic solution, but the β -compound at a lower temperature than the α -acid.

C. S.

Aromatic Arsenic Compounds.—By A. MICHAELIS (*Deut. Chem. Ges. Ber.*, ix, 1566—1569).—The author showed in a former paper (*Berichte*, viii, 1316) that arsenious chloride by its action on mercury diphenyl, produced *phenyl-arseniochloride*, $C_6H_5AsCl_2$. He has since found that, by using three or four times the theoretical quantity of arsenious chloride, the reaction may be made to take place at ordinary temperatures, according to the equation—



Phenyl-arseniochloride is a colourless liquid which refracts light strongly, and is not very mobile. It fumes in the air, and boils at $252-255^\circ$. It has a faint unpleasant smell in the cold, but a sharp penetrating odour when warm. It exerts a violent corrosive action on the skin. It is not altered by boiling water, but is dissolved by alkalis. The compound formed with them can be separated from the (potassium) chloride, as it is soluble in absolute alcohol. The compound is in all probability a salt $C_6H_5As(OK)_2$. By heating this salt with concentrated hydrochloric acid, phenyl-arseniochloride is reproduced. By employing hydrobromic or hydriodic acid instead of hydrochloric acid, phenyl-arsenio bromide and iodide may be prepared.

Phenyl-arseniotetrachloride, $C_6H_5AsCl_4$.—This body is easily prepared by addition of chlorine. It is a liquid which is decomposed by water, with formation of a solid oxychloride. Addition of more water produces—

Monophenyl-arsenic acid, $C_6H_5AsO(OH)_2$.—This body crystallises in long white needles, and is very soluble in hot water. It melts at 168° . When this acid is neutralised with ammonia, the addition of silver nitrate throws down silver monophenylarsenate, $C_6H_5AsO(OAg)_2$, as a white precipitate soluble with difficulty in water. It is easily soluble in ammonia and nitric acid.

Diphenyl-arseniochloride (phenylcacodyl chloride), $(C_6H_5)_2AsCl$.—During the fractional distillation of monophenyl-arseniochloride, a residue with higher boiling point is left behind. When purified it forms a thick oily liquid. It does not fume in air, and is almost inodorous. Its boiling point is higher than that of mercury. It is not altered by, and is heavier than water.

Diphenyl-arseniotrichloride (phenylcacodyl trichloride) $(C_6H_5)_2AsCl_3$.—Diphenyl-arseniochloride absorbs chlorine eagerly, and forms a solid trichloride, which has a yellow colour, resembling phosphorus pentachloride, but it is more stable than this body in presence of damp air and water. It melts at 174° , and solidifies in crystals. It is decomposed by warm water, with formation of a liquid, probably an oxychloride, which suffers further decomposition on boiling.

Diphenyl-arsinic acid (phenylcacodylic acid), $(C_6H_5)_2AsO(OH)_2$, separates on cooling the filtrate when the last body is decomposed by

water. It consists of fine needles, which dissolve with difficulty in cold, easily in hot water. It melts at 174° . The solution neutralised with ammonia gives on addition of silver nitrate a white precipitate of silver diphenylarsinate $(C_6H_5)_2AsO(OAg)$, which is soluble in ammonia and nitric acid. The diphenyl-arsenic compounds correspond with the cacodyl compounds of the fatty acid series. The further examination of these compounds, and the preparation of the corresponding antimony and bismuth compounds, will be immediately undertaken.

G. T. A.

New Method of Preparing Benzenesulphinic and Toluene-sulphinic Acids. By R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1584—1587).—Benzenesulphinic acid, $C_6H_5SO_2H$, is readily obtained by adding zinc-dust to a cooled alcoholic solution of the chloride of benzenesulphonic acid. The zinc salt thus obtained is well washed with water, in which it is almost insoluble, and then decomposed by sodium carbonate. The solution thus obtained is concentrated and mixed in the cold with hydrochloric acid, which precipitates the benzene-sulphinic acid. In a similar way toluenesulphinic acid may be obtained.

Benzenesulphinic acid is also obtained by adding a little water to a few drops of benzenesulphonic chloride and then mixing with zinc dust. After some time a brisk reaction sets in, and the zinc salt separates out. More zinc-dust and chloride are now alternately added, care being taken to have the former always in excess. The corresponding toluene compound may also be prepared by an analogous process.

The zinc salts of the two acids crystallise from hot water in small nacreous plates, having the composition $(C_6H_5SO_2)_2Zn + H_2O$ and $(C_6H_4CH_3SO_2)_2Zn + H_2O$.

C. S.

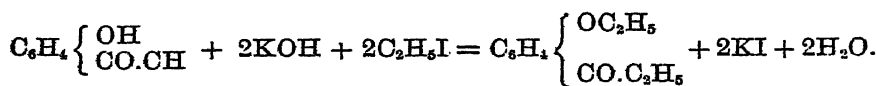
Benzenedisulphinic Acid. By C. PAULY (*Deut. Chem. Ges. Ber.*, ix, 1595).—This compound is formed by the action of zinc dust on a mixture of benzenemetadisulphonic chloride and water. The zinc salt thus formed was decomposed with potassium carbonate, the solution concentrated, and decomposed with hydrochloric acid. On shaking this liquid with ether, three layers were formed, the middle one consisting of the disulphinic acid, $C_6H_4(SO_2H)_2$, which is almost insoluble in ether but freely soluble in water. Its solution first reddens litmus and then bleaches it, and is easily changed when exposed to the air.

C. S.

Resorcindisulphonic Acid. By J. PICCARD and A. HUMBERT (*Deut. Chem. Ges. Ber.*, ix, 1479—1483). This compound is formed by adding one part of resorcin to ten parts of concentrated sulphuric acid. At 150° — 160° , crystals separate out, which are dissolved by heating to 190° — 200° . On cooling the disulphonic acid, larger crystals are formed, which are deliquescent, freely soluble in water and alcohol, and give with ferric chloride a ruby-red colour. When its solution is saturated with chalk a neutral calcium salt is obtained which crystallises well, whereas on using milk of lime, a basic salt is formed, which is very soluble and does not crystallise well. On adding to a hot solution of one of these salts a solution of barium chloride, a white crystalline

precipitate, $\text{C}_6\text{H}_4 \left\{ \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \right\} \text{Ba}$, is obtained. By the action of bromine on the free acid tribromoresorcin is formed. C. S.

Ethyl-compounds of Salicylic Acid. By C. GÖTTIG (*Deut. Chem. Ges. Ber.*, ix, 1473—1475). *Monethylic salicylate*, $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{C}_2\text{H}_5$, is readily formed by passing hydrochloric acid into an alcoholic solution of the acid as long as it is absorbed. It is an oily liquid boiling at 226° — 228° , and identical with that obtained by distilling salicylic acid with a mixture of alcohol and sulphuric acid. When its potassium phenate is heated with ethyl iodide to 160° , the diethylic ether, $\text{C}_6\text{H}_4(\text{OC}_2\text{H}_5)_2$, is obtained. The same compound is formed by heating salicylic acid with potash and ethyl iodide in the proportions indicated by the following equation:—

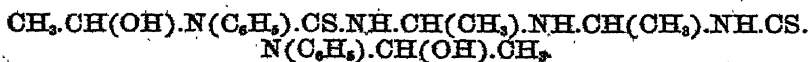


It is a colourless liquid boiling at 160° — 165° , and smelling like oil of wintergreen. C. S.

A Series of Compounds derived from Aldehyde-ammonia. By R. SCHIFF (*Gazzetta chimica italiana*, vi, 244—255). On heating to 80° an alcoholic solution containing 1 mol. of phenyl thiocyanate and 2 of aldehyde ammonia, and allowing the mixture to cool, a voluminous white crystalline precipitate is obtained if sufficient alcohol has been employed. This crystallises in silvery-white needles and has the composition $\text{C}_{22}\text{H}_{31}\text{N}_5\text{O}_2\text{S}_2$. As it has been found that water and ammonia are eliminated in this reaction, it is most probably that represented by the equation—



From the results of Nencki's investigation of the action of aldehyde ammonia on thio-carbamide (sulphurea), it is not improbable that the constitutional formula of the body is—



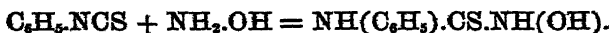
The substance is not decomposed by dilute acids in the cold, but on boiling it with them, aldehyde is eliminated. It has a bitter taste resembling that of quinine sulphate. When the thiocarbanilo-ammon-aldehyde is heated to 150° with concentrated hydrochloric acid, it is decomposed with formation of aldehyde, hydrogen sulphide, and carbonic anhydride, besides ammonia and aniline. Heated with excess of acetic anhydride at 100° yields aldehyde and *acetylphenyl-thiocarbamide*, $\text{C}_6\text{H}_5\text{N}_2\text{OS}$ or $\text{C}_6\text{H}_5.\text{NH.CS.NH.C}_2\text{H}_5\text{O}$. It crystallises in large iridescent plates.

On treating allyl thiocyanate with aldehyde-ammonia as above described, a corresponding allyl compound, $\text{C}_{16}\text{H}_{31}\text{N}_5\text{S}_2\text{O}_2$, is obtained which melts at 107° — 108° and is readily soluble in chloroform,

alcohol, or warm water, but when its aqueous solution is boiled decomposition takes place with elimination of aldehyde. The residue on evaporation yields a dense syrup of a red colour, which deposits crystals of allylthiosinamine, $C_3H_5.NH.CS.NH_2$, on standing. When the allyl-compound is heated to 150° with concentrated hydrochloric acid allylamine is formed amongst other products.

The action of aldehyde-ammonia on ethylic thiocyanate also yields a crystalline compound. It forms silvery needles which melt without decomposition at 118° — 119° . Its formula is analogous to that of the phenyl-compounds previously described. It is exceedingly soluble in alcohol, ether, chloroform, and hot water, somewhat less so in cold water.

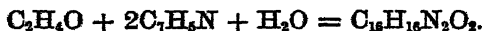
The author has also made experiments for the purpose of obtaining an oxythiocarbamide by acting on thiocarbamilide with a solution of hydroxylamine.



A different reaction took place however, for on gently warming the liquid the whole of the sulphur was precipitated in the free state and a substance was formed which crystallises in needles. It is not improbable that the hydroxylamine, ordinarily a powerful reducing agent, here has an oxidising action similar to that which takes place when aldehyde, in contact with it, is converted into acetic acid.

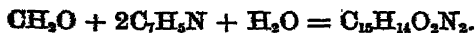
C. E. G.

Some Aldehyde-compounds. By E. HEPP and G. SPIESS (*Deut. Chem. Ger. Ber.*, ix, 1424—1429). On dissolving 1— $1\frac{1}{2}$ per cent. of paraldehyde in cold sulphuric acid, carefully adding benzonitril and then water, after some hours a white powder separates out, crystallising from alcohol in long needles melting at 204° . This body is formed according to the equation—



Alkalis and acids resolve it into aldehyde and benzoic acid, and the compound is therefore *ethidenedibenzamide*, $CH_2.CH(NH.CO.C_6H_5)_2$; which Nencki obtained by the action of aldehyde on benzamide, and Lämprich, who was unable to explain its constitution, by treating aldehyde-ammonia with benzoyl-chloride. The authors cannot explain how in the above reaction the addition of 1 mol. of water takes place.

When a mixture of equal volumes of benzonitril and chloroform is treated with sulphuric acid and methylal is gradually added, a reaction takes place which must be moderated by cooling—



The *methenedibenzamide*, $CH_2(NH.CO.C_6H_5)_2$, thus formed crystallises from alcohol in needles melting at 212° .

Chloral and benzonitril yield *trichlorethidenedibenzamide*, $CCl_3.CH(NH.CO.C_6H_5)_2$, crystallising from alcohol in needles melting at about 210° , and which are decomposed at a higher temperature, while the two other compounds can be sublimed. Similar compounds are

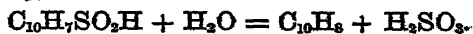
formed by bromal, butyryl-chloral, valeraldehyde, but not by benzaldehyde. C. S.

Artificial Oil of Bitter Almonds. By E. LIPPMANN and J. HAWLICZEK (*Deut. Chem. Ges. Ber.*, ix, 1461—1463). The oil obtained artificially from toluene is identical with the natural. C. S.

Nitrobenzoyl. By E. LIPPMANN and J. HAWLICZEK (*Deut. Chem. Ges. Ber.*, ix, 1463—1465). When 20 volumes of a mixture of 1 of nitric acid and 2 of sulphuric acid are gradually added to 1 volume of oil of bitter almonds, a solid and a liquid product are formed. The former is metanitrobenzaldehyde, which when quite pure forms small white needles, melting at 58° and forming with acid sodium sulphite a crystalline compound. The isomeric liquid body does not combine with this salt; it is a heavy, thick, yellow oil, which cannot be distilled even in a vacuum, and is converted by oxidising agents into benzoic acid; it is therefore nitrobenzoyl, $C_6H_5CO.NO_2$. C. S.

On the Naphthalene-sulphinic Acids. By E. GESSNER (*Deut. Chem. Ges. Ber.*, ix, 1500—1505). *α -Naphthalene-sulphinic Acid*, $C_{10}H_7SO_2H$.—A solution of the α -naphthalene sulphonie chloride in absolute ether was gradually treated in a retort with sodium amalgam until an excess of the latter remained, the retort with condenser being arranged so as to cause the return of all condensed products. Heat was applied till a sample of the solution left no residue on evaporation; ten to twelve hours are generally required for this. The reaction being completed, the ether is distilled off, and the residue, consisting of the sodium-compound of the α -sulphinic acid and sodium chloride, is dissolved in a moderate quantity of water, hydrochloric acid is added in excess, and the solution concentrated by evaporation. On cooling and standing for several hours, most of the α -naphthalenesulphinic acid separates out as a crusty mass. To purify the discoloured acid its barium salt is repeatedly prepared and decomposed by dilute sulphuric acid, the precipitated barium sulphate retaining each time a portion of the colouring matter. Lastly, the aqueous solution of the acid is boiled with lead carbonate, filtered, and the resulting lead salt decomposed by hydrogen sulphide. The precipitated sulphide carries down with it all remaining impurities, so that the evaporated filtrate now yields the pure white crystalline sulphinic acid. The pure acid forms beautiful white, shining scales, which melt at high temperatures, dissolve with difficulty in water containing hydrochloric acid, much more easily in pure water, with moderate facility in alcohol, and sparingly in ether.

The sulphinic acid is decomposed at 180° by dilute hydrochloric acid, with formation of naphthalene and sulphurous acid (sulphur dioxide and water),



In aqueous solution the α -naphthalene sulphinic acid combines directly with bromine, and appears to form a brominated sulphinic acid.

The salts of α -acid form silky scales or needles, and are for the most part easily soluble in water and alcohol.

α -Potassium salt (potassium sulphinaphthalate), $C_{10}H_7SO_2K + \frac{1}{2}H_2O$.—Small, white, silky scales, which in concentrated aqueous solutions form stellated groups.

α -Barium salt ($C_{10}H_7SO_2$)₂Ba + $1\frac{1}{2}H_2O$.—Fine, silky needles, only slightly soluble. 1 part of salt dissolves in 201 parts of water at 14° and in 50 parts of boiling water.

α -Lead salt ($C_{10}H_7SO_2$)₂Pb + H_2O .—The water is given up at 200° , the salt becoming greyish. The salt crystallises from aqueous solutions in long, branching, silky needles; it is also soluble in alcohol.

α -Silver salt, $C_{10}H_7SO_2Ag$.—White scales, easily soluble in water and alcohol. Can be heated to 200° , or a higher temperature, without alteration.

β -Naphthalene-sulphinic Acid.—The β -naphthalene sulpho-chloride is easily acted on by sodium amalgam (in a pasty condition). With a concentrated ethereal solution the reaction is completed for the most part at ordinary temperatures, which is not the case with the α -compound. The decomposition took place completely after long heating on the water-bath. The sodium salt of the β -naphthalenesulphinic acid is obtained, together with sodium chloride, as a crystalline powder. It is easily extracted by alcohol and isolated. The aqueous solution of the salt treated with hydrochloric acid precipitates the β -sulphinic acid directly. It is a white, crystalline powder, nearly destitute of the glistening appearance characteristic of the α -substance. In alcohol, ether, and pure water the β -substance is not difficult to dissolve, but in dilute hydrochloric acid it dissolves but slowly. It melts at 105° and re-solidifies at 84 – 86° . The β -acid is more easily decomposed by dilute hydrochloric acid than the α -acid, viz., at 150° . Sulphur dioxide and naphthalene are liberated.

β -Potassium salt, $C_{10}H_7SO_2K + \frac{1}{2}H_2O$.—White, faintly glistening scales, easily soluble in alcohol, very soluble in water.

β -Barium salt, ($C_{10}H_7SO_2$)₂Ba.—White, faintly glistening, slightly soluble needles. 1 part of the salt requires 21.5 parts of water of 15° , or 16 parts of boiling water, for solution. It is more soluble than the α -compound.

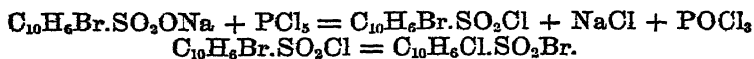
β -Calcium salt, ($C_{10}H_7SO_2$)₂Ca + $3H_2O$.—White, shining, crystalline powder, easily soluble in water and alcohol.

β -Magnesium salt, ($C_{10}H_7SO_2$)₂Mg + $6H_2O$.—Shining scales, more easily soluble in alcohol than in water.

When bromine vapours are passed over an aqueous solution of the β -naphthalenesulphinic acid, a white powder is separated, consisting of a bromine- β -naphthalenesulphinic acid. The barium salt of this acid forms a white granular powder, insoluble in alcohol, difficultly soluble in water. An estimation of the barium contained therein gave results required by the formula $(C_{10}H_6BrSO_2)_2Ba$.

Attempts to convert the chlorides of the isomeric naphthalenedisulphinic acids into the corresponding disulphinic acids were fruitless. An endeavour was made to obtain the bromonaphthalenesulphinic acid from the bromonaphthalene-sulphochloride by treatment with

sodium amalgam, just as Otto sought to do. The sodium salt of the bromonaphthalenesulphonic acid was treated with phosphorus pentachloride, whereby a sticky turpentine-like mass was obtained. This, by repeated boiling of its ethereal solution with animal charcoal, yielded a solid substance, which was repeatedly recrystallised from ether, and was finally obtained in beautiful white needles, melting at 115° — 116° . This turned out to be, however, a *chloro-naphthalene-sulphobromide*, and not the expected bromo-naphthalene sulphochloride. It is considered that, first, the bromosulphochloride is formed, and then, and on exchange of the halogen-atoms taking place, the chlorosulphobromide, thus—



Chloronaphthalene-sulphinic Acid, $\text{C}_{10}\text{H}_6\text{Cl}.\text{SO}_2\text{H}$.—The bromide just described was dissolved in absolute ether and treated with sodium amalgam. A lively reaction ensued in the cold, and a deposition of crystalline substance took place. After treatment with water, decomposition with hydrochloric acid, evaporation to dryness, and solution in alcohol, a free halogen-sulphinic acid was obtained. By evaporating the alcoholic solution the sulphinic acid separated partly in crusts, partly in an oily condition. It was purified by repeated preparation of its barium salt, and decomposition of this salt by dilute sulphuric acid, and was finally obtained in delicate needles by crystallising from alcohol.

A substance, in small quantity, was crystallised out of the alcoholic mother-liquors from the crude oily chloro-naphthalenesulphinic acid in white, shining scales, and this was found to be a small quantity of α -naphthalenesulphinic acid. Its formation was due to the presence of traces of moisture.

Barium Chloronaphthalenesulphite, $(\text{C}_{10}\text{H}_6\text{ClSO}_2)_2\text{Ba} + 1\frac{1}{2}\text{H}_2\text{O}$.—Prepared by adding barium chloride to an aqueous solution of the chloro-naphthalenesulphinic acid; at first a milky turbidity arises, and after some time a precipitate, which crystallises from boiling water in shining scales, and is the pure barium salt. This compound is almost insoluble in alcohol. W. S.

Some Derivatives of α - and β -Naphthoic Acid. By O. HAUSAMANN (*Deut. Chem. Ges. Ber.*, ix, 1513—1523).— *β -Naphthoic*

anhydride, $\beta.\text{C}_{10}\text{H}_7\text{CO}$ $\left. \begin{array}{l} \text{O} \\ \text{O} \end{array} \right\}$ —Equivalent quantities of β -naphthoyl

chloride and calcium β -naphthoate dried at 120° , were heated so long at 150° — 160° , that the odour of naphthoyl chloride had disappeared. The product was pulverised, washed with water to remove calcium chloride, dried, and finally recrystallised from benzene and ether. Beautiful silky plates or needles are thereby obtained, melting at 133° — 134° . The body is very soluble in hot benzene, soluble in hot ether, slightly in cold ether. Boiling water converts the anhydride gradually into the β -naphthoic acid; boiling alcohol into the ethyl ether of the acid.

α - β -Naphthoic anhydride, $\begin{matrix} \alpha \cdot C_{10}H_7CO \\ \beta \cdot C_{10}H_7CO \end{matrix} \rangle O$.—Prepared by the same process as the β_2 anhydride, from the α -naphthoyl chloride and the potassium β -naphthoate. It resembles the β_2 compound, and crystallises in delicate needles, melting at 126°, and, when once fused, remains fluid for a long time.

β_2 -Dinaphthylketone, $\begin{matrix} \beta \cdot C_{10}H_7 \\ \beta \cdot C_{10}H_7 \end{matrix} \rangle CO$.—This ketone was prepared by distilling dry calcium β -naphthoate. Naphthalene first passed over, and then a reddish-brown oil, which quickly solidified. This mass was redistilled, giving a yellow crystalline mass, which, by recrystallising from chloroform and ether, yielded white silky leaflets. It melts at 164°—164°.5. It dissolves easily in chloroform, with difficulty in alcohol, and more in ether. Mixed with soda-lime and heated in a tube from 300°—350°, it gave naphthalene and β -naphthoic acid.

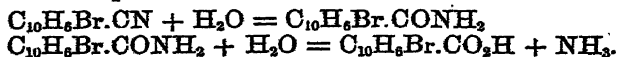
Brom- α -Cyannaphthalene, $C_{10}H_6BrCN$.— *α -Cyannaphthalene* was dissolved in carbon disulphide, and the right proportion of bromine gradually added, hydrobromic acid being meanwhile liberated. The mass was now heated till no more hydrobromic acid was liberated, and the carbon disulphide distilled off, when a fluid residue remained, soon solidifying. The mass washed and digested with cold alcohol, left a fine white powder. By recrystallising this from hot ether, chloroform, or glacial acetic acid, yellow needles were obtained; these, by sublimation, were obtained quite white. Melting point = 147°.

Strongly heated, the brominated nitril decomposes, with liberation of ammonia.

Brom- β -Cyannaphthalene, $\beta \cdot C_{10}H_6BrCN$.—Prepared and purified in the same manner as the α -compound. Beautiful white, broad needles. Melting point = 148°—149°. By chloroform and benzene it is easily dissolved, only slightly by cold ether, spirits of wine and glacial acetic acid, but readily by the same liquids when hot.

Brom- α -Naphthoic acid $\alpha \cdot C_{10}H_6BrCO_2H$.—The α -bromocyanide was heated for several hours to 140°—150° with alcoholic sodium hydrate. The reaction was so completed that, after driving off the alcohol, the mass remaining was quite dissolved by water. In this solution, hydrochloric acid in excess produces a white flocculent precipitate, which, after washing and drying, was recrystallised from hot alcohol or glacial acetic acid, yielding white crystalline grains, and, on sublimation, needles melting at 142°. This acid does not dissolve appreciably in boiling water; it dissolves slightly in cold alcohol, ether, and glacial acetic acid; with moderate facility in the three latter liquids, if they are hot; easily in benzene. By heating the brom- α -cyanonaphthalene with soda for a long time, a brominated naphthamide is obtained, in yellow flocks, crystallising from hot alcohol in yellow needles. By several crystallisations the body is obtained in white needles, melting at 240°—241°. This body is insoluble in alcohol and alkalis, soluble in boiling alcohol and ether. By further heating with soda-lime, ammonia is set free. From a bromine determination, it is considered to have the formula $C_{10}H_6BrCONH_2$.

Monobromonaphthamide, $C_{10}H_7Br.CONH_2$.—By still more strongly heating with dilute hydrochloric acid or alcoholic potash, ammonia and the brom- α -naphthoic acid, melting at 242° , are obtained. The so-called saponification process of the brom- α -cyanaphthalene indicates two distinct phases of the reaction:—

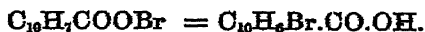
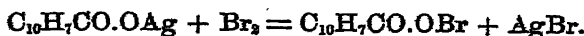


Brom- β -naphthoic acid, β . $C_{10}H_7Br.CO_2H$.—This acid was prepared from the brom- β -cyanaphthalene exactly as the brom- α -naphthoic acid was prepared from the brom- α -cyanide. The brominated β -acid separates from alcohol or glacial acetic acid in white grains, subliming in beautiful needles, melting at 256° .

The brom- β -naphthoic acid is scarcely soluble in boiling water; slightly soluble in alcohol, ether, and glacial acetic acid when cold; easily in the same liquids when hot. From the brom- β -cyanaphthalene also a body was obtained, which is, doubtless, brom- β -naphthamide. By fusion with caustic alkali, both bromonaphthoic acids were attacked, and new crystallisable acids formed, doubtless oxynaphthoic acids. The isomeric bromonaphthoic acids were also directly prepared from the naphthoic acids, in the same manner as bromobenzoic acid is obtained from benzoic acid.

Monobromonaphthoic Acids from the Silver-Naphthoates by means of Bromine.—The silver salts of both the naphthoic acids were placed in a closed vessel in the sunlight, or, in default thereof, in a warm place, and exposed to the action of bromine vapours, till no more absorption took place. The silver salts were extracted with ether, and the solutions evaporated; a yellow residue then remained, consisting in both cases, partly of a solid, partly of an oily body, which soon solidified. The crude acids thus obtained were dissolved in soda-solution; the solutions decolorised with animal charcoal, and then precipitated with barium chloride. The barium salts were dissolved in boiling water, and, on addition of hydrochloric acid, the isomeric bromonaphthoic acids were precipitated in yellow flocks. By repeated recrystallisation from glacial acetic acid and sublimation, the acids were obtained in white needles. The α -acid melted at 242° ; the β -acid at 256° .

The formation of these acids is thus illustrated:—



The above acids were also obtained by heating the one or other of the naphthoic acids with bromine and water for 8–10 hours, at 150° – 160° . The easiest method, and the one giving the best yield, is as follows:—One or other of the naphthoic acids is dissolved in a little boiling acetic acid, and to the hot solution the equivalent proportion of bromine is added, together with a little iodine. On cooling the solution, the crude acids crystallise out, and are purified by one recrystallisation. By this method these isomeric monobromonaphthoic acids may easily be obtained in quantity. The salts of these acids are, as a rule, less soluble than the corresponding naphthoates, and at 150° lose all their water of crystallisation.

The barium and calcium salts dissolve in hot water with difficulty, but when they are once dissolved, the solutions must be strongly evaporated before separation takes place.

α-Potassium salt, $C_{10}H_5Br.CO.OK + \frac{1}{2}H_2O$.—Amorphous white mass, easily soluble in water; insoluble in alcohol and ether.

β-Potassium salt, $C_{10}H_5Br.CO.OK + 2\frac{1}{2}H_2O$.—Amorphous, and rather more soluble in water than the *α*-compound.

α-Calcium salt, $C_{10}H_5Br.CO.O \left\{ \begin{array}{l} Ca + 1\frac{1}{2}H_2O. \text{—Crystallises in fine} \\ C_{10}H_5Br.CO.O \end{array} \right.$
white grains. Soluble in $66\frac{1}{2}$ parts of water at 20° .

β-Calcium salt, $C_{10}H_5Br.CO.O \left\{ \begin{array}{l} Ca + 3H_2O. \text{—White granules, re-} \\ C_{10}H_5Br.CO.O \end{array} \right.$
quiring 5,000 parts of water at 20° , for solution.

α-Barium salt, $C_{10}H_5Br.CO.O \left\{ \begin{array}{l} Ba + 3H_2O. \text{—Crystallises in beau-} \\ C_{10}H_5Br.CO.O \end{array} \right.$
tiful white needles. Soluble in 59 parts of water at 21° .

β-Barium salt, $C_{10}H_5Br.CO.O \left\{ \begin{array}{l} Ba + 3H_2O. \text{— Beautiful needles,} \\ C_{10}H_5Br.CO.O \end{array} \right.$
soluble in 4,300 parts of water at 21° .

Silver salts, $C_{10}H_5Br.CO.OAg$.—Obtained as flocculent precipitates, forming, when dried, white anhydrous powders.

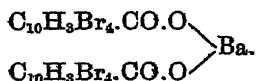
Tribromo-β-Naphthoic acid, $C_{10}H_4Br_3.CO.OH$.—*β*-naphthoic acid was gradually heated in sealed tubes to about 350° , with iodised bromine, the tubes being occasionally opened to let out hydrobromic acid. Slight decomposition ensues at the above temperature, naphthalene and carbon dioxide being formed. A brown solid mass is thus obtained, which is finely pulverised, and repeatedly boiled with dilute ammonia, in which (as well as soda and potash) it is soluble with difficulty, especially if the alkalis are in excess. By saturating the clear ammoniacal extract with hydrochloric acid, yellowish-brown flocks are precipitated. These were washed, and re-dissolved in boiling dilute ammonia. On cooling, small silky needles of the ammonium salt were obtained. By hydrochloric acid the brominated acid separated out, and was then re-crystallised from hot glacial acetic acid. This acid is soluble with some difficulty in cold alcohol, ether, or glacial acetic acid, far more soluble on heating. On cooling, it separates in white grains. In water it is almost insoluble. The acid melts at 269° to 270° , and sublimes in fine needles, the residue partially carbonising. The yield of acid, owing to the splitting up of the reaction on brominating, is not great. The ammonium, potassium, and sodium compounds form beautiful needles or leaflets, almost insoluble in cold water, with difficulty in hot.

The barium compound, $C_{10}H_4Br_3.CO.O \left\{ \begin{array}{l} Ba, \text{ was obtained, by pre-} \\ C_{10}H_4Br_3.CO.O \end{array} \right.$
cipitating the ammonium salt with barium chloride, as a white anhydrous powder, insoluble in water.

Tetrabromo- α - and β -naphthoic acids.—One molecule of naphthoic acid was gradually heated to 350° with 4—5 molecules of bromine, and some iodine. Carbon dioxide and bromonaphthalenes were formed, and a mass obtained, which was extracted with dilute ammonia or sodium hydrate; the dissolved acids were precipitated by hydrochloric acid, and purified by recrystallisation from boiling alcohol and glacial acetic acid. Thus were obtained

Tetrabromo- α -naphthoic acid, $C_{10}H_3Br_4.COOH$. — Small granular crystals, melting at 239°, and subliming in fine needles, often grouped in down-like masses. This acid dissolves best in glacial acetic acid. In boiling alcohol and ether it is moderately soluble, scarcely at all in cold benzene. Insoluble in pure water; dissolves in alkaline water with difficulty.

The tetrabromo- β -naphthoic acid melts at 259° to 260°, and sublimes in fine needles, with partial carbonisation. Glacial acetic acid is its best solvent. By precipitating the α - and β -ammonium salts with barium chloride, the barium salts were obtained. They are white powders, insoluble in water. After drying at 120°, they possess the following formula:—



The author is now investigating the oxidation-products of the bromo-naphthoic acids. W. S.

Synthesis of Indigo-Blue. By A. EMMERLING and C. ENGLER (*Deut. Chem. Ges. Ber.*, ix, 1422—1424).—The authors obtained some years ago traces of indigotin from nitro-acetophenone; but Wichelhaus, on repeating these experiments, got none. The nitro-compound which the authors used was a syrupy liquid, and remained so for weeks; they have since tried to obtain it again, but without success. But even the syrupy nitro-product did not always yield indigo-blue, the formation of which seems to depend on a certain temperature, on the kind of zinc-dust used, and so on. If the authors had known that in continuing their investigation they would encounter so many difficulties, they would not have published their first results.

Indigotin can, however, be obtained from indol, which, as Baeyer and one of the authors have shown, can be obtained synthetically from nitrocianamic acid. C. S.

Preparation of Indol. By C. ENGLER and JANECKE (*Deut. Chem. Ges. Ber.*, ix, 1411—1414).—Kühne has shown that indol is formed when albumin is distilled with potash. On using this method the authors found that blood and egg-albumin yield 0.25 per cent., casein and gluten only 0.1 per cent., and gelatin and keratin only traces. From this it appears that the yield is the smaller the more loosely-combined nitrogen the proteid contains; but on distilling with potash the residues of blood-albumin after its treatment with baryta or hydrochloric acid, hardly any indol was formed. C. S.

Properties of Indol. By C. ENGLER and JANECKE (*Deut. Chem. Ges. Ber.*, ix, 1414—1419).—Nencki has shown that indol obtained by the pancreatic fermentation of proteids yields indigotin (besides other bodies) when treated with ozone. Indol from indigo behaves in the same way, while that obtained by heating albumin with potash does not give a trace by this method. The two compounds differ also by their melting points; indigo-indol melts at 52°; albumin-indol, after repeated crystallisation from water, at 85—86°. Both compounds have, however, the same molecular formula and the same characteristic smell. From this it appears probable that the true indol, which is an ortho-compound, is converted by fusion with potash, into the isomeric *pseudo-indol*. C. S.

Rosaniline and Fuchsine. By A. WURTZ (*J. Pharm. Chim.* [4], xxiv, 18—24).—This paper describes the industrial preparation of fuchsine by the ordinary processes, and also by Coupier's process, in which no arsenical compounds are employed. In this, crude aniline, nitrobenzene, hydrochloric acid, and iron are heated together. The iron acts as a carrier of oxygen from the nitrobenzene to the aniline. The product contains 25 per cent. of aniline; but after it has been treated with water and saturated with lime, the aniline is distilled off with the water; while the calcium chloride, which is formed by the addition of the lime, precipitates the hydrochloride of rosaniline.

R. R.

Effect of Temperature on the Power of Solutions of Quinine to Rotate Polarised Light. Suggestions regarding the Preparation to be used when Quinine is employed as a Medicine. By JOHN C. DRAPER (*Amer. J. of Sci.* [3], xi, 42—47).—The polariscope employed by Prof. Draper in these experiments was fitted with a glass tube 220 mm. in length; this tube was provided with a water jacket which could be maintained at any given temperature; the observations were made with the sodium flame. The quinine used, was the pure alkaloid carefully dried over sulphuric acid; of this 1 gram was dissolved in 50 c.c. of 97 per cent. alcohol.

The average of 200 observations on four such solutions at 25° C. gave $\alpha = -6.789^\circ$, whence

$$[\alpha]_D = \frac{\alpha \times V}{\lambda \times p} \times 100 = \frac{-6.789 \times 50}{220 \times 1} \times 100 = -154.30^\circ.$$

The average of 200 observations on the same solutions at 47° C. gave $\alpha = -6.245^\circ$ and $[\alpha]_D = -141.93^\circ$, it follows that for a rise of temperature of 1 degree $[\alpha]_D$ decreases 0.562.

Effect of Variation in the Proportion of Alcohol in the Solution.—A solution similar to the above was prepared, and 100 readings made at temperatures between 20° and 50°, the mean value of α was -6.05° at 35°; the solution was then diluted with 50 c.c. of the same alcohol. The average of 100 readings at similar temperatures was $\alpha = -2.61^\circ$ at 36°. This second solution was then diluted again with 100 c.c. of

alcohol; the mean of 100 readings was now $\alpha = -1.27^\circ$ at 36° . From these values we obtain—

For the first solution	$[\alpha]_D = -137.50^\circ$ at 35°
„ second „	$[\alpha]_D = -118.64^\circ$ at 36°
„ third „	$[\alpha]_D = -115.45^\circ$ at 36° .

Hence the dilution by alcohol of the solution of quinine lessens its power of rotation.

Experiments on a series of solutions made with undried quinine gave the same result.

Quinine combined with Sulphuric Acid.—The solution was made by placing one gram of dried quinine in 30 c.c. of water, adding just sufficient sulphuric acid to dissolve it, and then making up to 50 c.c. with distilled water. The results were—

$$\begin{aligned} [\alpha]_D &= -258.18^\circ \text{ at } 21^\circ \\ [\alpha]_D &= -243.86^\circ \text{ at } 43^\circ. \end{aligned}$$

One degree therefore causes a difference of 0.65° in rotation.

Effect of Variation in the Proportion of Water.—The solution was diluted to the same extent as in the previous experiments with quinine and alcohol, the results were as follows:—

For the first solution	$[\alpha]_D = -250.70^\circ$ at $31\frac{1}{2}^\circ$
„ second „	$[\alpha]_D = -235.45^\circ$ at 32°
„ third „	$[\alpha]_D = -234.54^\circ$ at $31\frac{1}{2}^\circ$.

The conclusions which may be drawn are—

(a.) Union with the acid imparts to the alkaloid a greatly increased power of rotation.

(b.) The aqueous solution of sulphate shows the same changes under the influence of temperature as the alcoholic solution of the alkaloid.

(c.) In both dilution causes diminished rotation.

Since the rotatory power of quinine is so much increased by union with acid, may not its physiological action be also increased, and the sulphate be a more powerful and certain medicine than the pure alkaloid?

F. D. B.

Transformation of the three Bromocinchonines into the Corresponding Oxybases. By A. KOPF (*Arch. Pharm.* [3], ix, 34—41).—By treating the three bromine derivatives of cinchonine— $C_{20}H_{23}BrN_2O$; $C_{20}H_{23}Br_2N_2O_2$; and $C_{20}H_{23}Br_3N_2O$ —with caustic potash, the three following oxybases have been obtained, viz., $C_{20}H_{24}N_2O$; $C_{20}H_{24}N_2O_2(OH)_2$; and $C_{20}H_{24}N_2O_3$.

These substances, when dissolved in a mixture of 2 vols. chloroform and 98 per cent. alcohol, rotate the polarised ray to the right, but not to so great an extent in cinchonine itself. M. M. P. M.

On an Alkaloid found in Damaged Turkey Corn and in Mildewed Maize Bread. By T. BRUGNATELLI and E. ZENONI (*Gazzetta chimica italiana*, vi, 240—244).—In the lower parts of Lom-

bardy it had been observed that the peasants were very subject to a fatal disease, *pellagra*, which slowly destroyed the vital powers. As it was known that those who were attacked lived chiefly on maize bread, which becomes mildewed with extraordinary rapidity, it was natural that the origin of the malady should be sought for in the bread. Lombroso found that an extract of maize bread attacked by *Penicillium Mâdis* induced in animals symptoms analogous to those of pellagra, and Duprè obtained from damaged maize a substance which gave the reactions of an alkaloid.

From the singularity of the facts hitherto observed, the authors were led to undertake an investigation of the subject, and for this purpose a considerable quantity of maize bread was allowed to become mildewed, and one portion examined immediately after the fungus had begun to appear, whilst another was left until the fungus was completely developed in every part. An alkaloid was obtained in both cases, but it was far more abundant in the latter. The alkaloid was extracted by Otto's modification of Stass's method. The ethereal solution on evaporation left a white or slightly yellowish residue, which quickly became coloured, especially when heated. It is insoluble in water, but soluble in dilute acids, being thrown down again by alkalis or alkaline carbonates as a white flocculent precipitate. It is soluble in alcohol and in ether, the ethereal solution yielding a white precipitate with an ethereal solution of tartaric acid. The free alkaloid has a very bitter taste, and contains nitrogen, but is so readily alterable that no analysis could be made of it. A solution of the alkaloid in concentrated sulphuric acid gives with oxidising agents an intense blue coloration very similar to that obtained with strychnine; it is distinguished from the latter, however, by the beautiful violet colour which is produced by the action of bromine vapour on its sulphuric acid solution. Ferric salts are without action on the alkaloid.

C. E. G.

Jaborandi (*Pilocarpus pinnatus*). By ERNEST HARDY (*J. Pharm. Chim.* [4], xxiii, 95—100).—The physiological action of an infusion of the leaves or stem of *Pilocarpus pinnatus* on the glands, heart, and pupil is opposite to that of atropine. A dose of 3 or 4 grams diminishes the amount of urine, lowers the proportion of urea in the urine, raises its percentage of urea, and increases perspiration.

The author has extracted from this plant an alkaloid which he calls *pilocarpine*, and which appears to be its active principle, by the following processes:—An aqueous, and then an alcoholic extract of the leaves and stems is diluted with water and precipitated with ammoniacal lead acetate; the liquid is filtered; the excess of lead removed with sulphuretted hydrogen; and the uncrystallisable acetate of pilocarpine obtained by evaporating the filtrate. On addition of mercuric chloride an insoluble double salt is formed; the mercury is removed with sulphuretted hydrogen, and the hydrochloride of pilocarpine decomposed by addition of ammonia in presence of chloroform; the chloroform, on evaporation, leaves pure pilocarpine.

Another method is to evaporate the infusion of the leaves of the plant to a syrup, mix with magnesia, evaporate to dryness, extract

with chloroform, evaporate the chloroform, add water, and finally evaporate in a vacuum.

Pilocarpine is a viscous substance giving crystallisable salts with hydrochloric, nitric, and sulphuric acids; the hydrochloride crystallises in long needles radiating from a common nucleus; it forms a double salt with platinic chloride.

Pilocarpine has a physiological action similar to that of the extract, and shows the same antagonism to the action of atropine.

The exposed heart of a frog, into the foot of which some solution was injected, ceased to beat, but recommenced on addition of some drops of atropine sulphate. In a similar manner the injection of a salt of atropine stopped a salivary flow produced by pilocarpine in a dog.

10 kilograms of the leaves of pilocarpus distilled with water, yielded 52 grams of a colourless transparent essence with fragrant smell. On fractionation it gave two liquids, one boiling at 178° and the other at 250° , and at a higher temperature a slightly greenish liquid, which solidified to a transparent mass. The essence, named pilocarpine, has the specific gravity 0.852 at 18° , and is a terpene, its formula being $C_{10}H_{16}$. Its rotatory power is $(\alpha)_D = 1.21$. When hydrochloric acid gas is passed through pilocarpine mixed with 4 or 5 times its volume of ether, it is rapidly absorbed, and yields a colourless crystalline product, melting at 49.5° , of the formula $C_{10}H_{16} \cdot 2HCl$. It crystallises at once if a small crystal of terebenthene hydrochloride be placed in its solution. With ferric chloride it gives a pink colour, which changes to violet, and finally to blue. A liquid hydrochloride of the same formula is produced at the same time, but no trace of camphor.

A mixture of the two hydrochlorides was treated with nitric acid in a small retort, according to Berthelot's process of testing for camphor. No ring appeared in the neck of the retort, showing that the hydrochloride contained no trace of camphor.

The essence of *pilocarpus* appears to resemble the isoterpenes, and to be analogous to essence of lemon.

W. R.

A Substance in Beer resembling Colchicine. By H. VAN GELDERN (*Arch. Pharm.* [3], ix, 32—33).—From a mixture of genuine hops and the gummy matter of beer a substance giving the reactions of colchicine was obtained: this substance was without poisonous action upon rabbits.

M. M. P. M.

Gelatin Considered as a Reducing Agent. By G. BIZIO (*Gazzetta chimica italiana*, vi, 255—258).—On adding an excess of mercuric chloride to a solution of gelatin acidulated with hydrochloric acid, a flocculent precipitate is produced which soon agglutinates and sinks to the bottom of the vessel as a dense layer. This swells up in pure water to a transparent jelly which subsequently dissolves. On adding potassium hydrate to this solution and allowing it to stand, metallic mercury is precipitated in a finely divided state as a grey powder: the reduction is greatly facilitated by heating the liquid to 100° . The solution of gelatin and mercuric chloride when allowed to stand for a month or more deposited mercurous chloride. On adding

potassium hydrate to a solution of gelatin mixed with a little freshly precipitated mercuric oxide until the latter was dissolved, and then heating as before, metallic mercury was deposited in a finely divided state. The mercuric chloride can be completely separated from the gelatin by submitting a solution of the precipitate to dialysis.

C. E. G.

Researches on Hæmatin. By P. CAZENEUVE (*J. Pharm. Chim.*, xxiv, 116—120).—The author prepares pure hæmatin by treating 1 litre of defibrinated blood with 2 litres of a mixture of 3 parts ether, and 2 parts alcohol of 85°. After 24 hours, the liquids having been stirred from time to time, the ethereal solution is decanted off and replaced by a fresh quantity of liquid containing 2 per cent. of oxalic acid. This dissolves out the colouring matters, and on the addition to it of ether holding ammonia gas in solution, to exact saturation of the oxalic acid, hæmatin is precipitated. The precipitate is washed successively with ether, alcohol, and water, and the residue is finally treated with ether saturated with hydrochloric, hydrobromic, or hydriodic acid, when it yields characteristic crystalline compounds. The formation of crystals of hydrochloride of hæmatin (the hemin of Teichmann) is an important indication for chemico-legal cases; and the paper describes the manipulation by which a blood-stain not larger than a pin's head may be made to yield the crystals by which the presence of blood may be proved.

R. R.

Essence of Achillea Ageratum (Linn.). By S. DE LUCA (*J. Pharm. Chim.* [4], xxiii, 105—106).—This plant grows in Italy and in Provence. It used to be recommended as a remedy for worms in children, but is now cultivated only as an ornament. When its leaves are rubbed between the hands, they emit an odour resembling that of camphor. It contains most essence before it flowers. The essence extracted by distillation with water has the specific gravity 0.849 at 24°. It boils at 165—182°, the thermometer remaining stationary between 180 and 182°. This fraction consists of a substance of the formula $C_{24}H_{44}O_2$. It is not oxidised by contact with oxygen, even in presence of platinum-black. It gives a milky emulsion with acid sodium sulphite, which becomes clear after several days. It does not solidify at -18° . With chlorine it turns slightly reddish, and on neutralisation of the hydrochloric acid with sodium carbonate and caustic potash, a brown insoluble liquid floats to the top. This liquid, after distillation, was left in contact with solid potassium hydrate, and the original essence was reproduced. The same result was obtained by treating the essence with bromine.

W. R.

Apiol. By E. v. GREICHTEN (*Deut. Chem. Ges. Ber.*, ix, 1477—1479).—Pure apiol or parsley-camphor forms long, white, brittle needles, melting at 30° and boiling at about 300° . On boiling it with alcoholic potash, it is converted into a body crystallising in pearly, rhombic plates melting at 53.5° and containing, as a mean of three combustions, $C = 65.4$, $H = 5.5$. On boiling it with dilute nitric acid,

it yields oxalic acid and a body crystallising from alcohol in long, brilliant, yellow needles melting at 114° and dissolving gradually in boiling potash with an intensely purple colour. C. S.

Physiological Chemistry.

On the Influence of Temperature on the Respiration of Cold-blooded Animals. (Introduction to the following Experimental Work of Hugo Schulz.) By E. PFLÜGER (*Pflüger's Archiv. f. Physiol.*, xiv, 73—77).—In this note the author criticises the experiments, few in number, on which depends the generally accepted theory that in cold-blooded animals the tissue-metamorphosis increases with the temperature. He finds that it rests only on a few general ideas, the most interesting of which is that there exists a certain lowest limit of temperature which does not kill the animals but suspends life, and for several months renders the consumption of oxygen and the excretion of carbonic acid *nil*. The estimation of this temperature he regards as one of the most important tasks. E. C. B.

On the Relation between Tissue-metamorphosis and Body-temperature in Amphibia. by HUGO SCHULZ (*Pflüger's Archiv. f. Physiol.*, xiv, 78—91).—The author describes at length the apparatus (resembling in principle that used by Regnault) by which he estimated the amount of carbonic acid excreted by frogs at different temperatures. The body-temperature of the frogs was taken before and after each experiment. Of these there were sixteen, lasting several hours each.

The result of all the experiments is:—That the tissue-metamorphosis of frogs stands in direct relation to their temperature. At a body-temperature of 1° the frog exhales so little carbonic acid, that it is not even certain that any is produced. The animal is no doubt at what Pflüger calls the limit of the dissociation-temperature (*i.e.* the temperature at which dissociation takes place); at from 33 to 35° C., however, the tissue-metamorphosis of the frog is as great as that of man, and would therefore at 37° probably greatly exceed the same, if the organism of the cold-blooded animal permitted so rapid a replacing of tissue as the great consumption requires. The upper limit of temperature for frogs is, he finds, about 35° . The figures resulting from the estimation of the oxygen prove the same law with equal certainty. E. C. B.

On the Influence of the Surrounding Temperature on the Tissue-metamorphosis of Warm-blooded Animals. By GIUSEPPE COLASANTI (*Pflüger's Archiv. f. Physiol.*, xiv, 92—124).—As the result of numerous experiments on guinea-pigs, conducted with every precaution to secure hermetic closure of the apparatus, which was a modification of that used by Regnault, the author arrived at the

following conclusions:—Guinea-pigs consume at a temperature of 18.8°C ., per kilo. of weight and per hour, 1127 c.c. (1.612 gram) of oxygen, and exhale 964.15 c.c. (1.896 gram) of carbonic acid. In guinea-pigs, under normal conditions, the average proportion between the oxygen contained in the exhaled carbonic acid and the oxygen absorbed = .86, and this proportion remains constant at different temperatures. With decrease of the temperature of the air a guinea-pig consumes for 1°C . per kilo. of weight and per hour 37.23 c.c. more oxygen, and gives off 33.66 c.c. more carbonic acid. In starving animals the proportion between the oxygen contained in the carbonic acid exhaled and the oxygen absorbed is smaller, but still constant at different temperatures. The author finds that in the starving state the temperature is regulated by the production of heat almost as energetically as in other conditions. His experiments confirm the fact that consumption of oxygen and formation of carbonic acid are a measure of the tissue-metamorphosis, and that the production of heat is proportional to the consumption of oxygen and the formation of carbonic acid. The increase of tissue-metamorphosis is by no means confined to the time immediately following the sinking of the temperature of the air, but occasionally increases so much after several hours that the internal temperature of the animal is considerably raised. During digestion guinea-pigs exhale marsh-gas and hydrogen, but not at all, or very slightly, when starving. The author thinks that guinea-pigs neither absorb nor exhale nitrogen, but does not speak with decision on this point.

E. C. B.

A Contribution to the Theory of Fever. By GUISEPPE COLASANTI (*Pflüger's Archiv. f. Physiol.*, xiv, 125—127).—During one of the experiments described in the last paper, a guinea-pig became feverish, and further experiments on this animal showed that on lowering the temperature of the air, there was only very slight increase in the consumption of oxygen and excretion of carbonic acid. The author also found that in the guinea-pig suffering from fever the tissue-metamorphosis considerably exceeded that of a normal animal, in spite of the former being in the starving state.

E. C. B.

Researches on the Bones of a Carnivorous Animal. By M. SCHRODT (*Landw. Versuchs.-Stat.*, xix, 349).—Aeby observed that, during the ignition of fossil-ivory, a certain amount of carbonic acid is expelled, which cannot afterwards be restored by treatment with ammonium carbonate, and he was led from this to regard bone-phosphate as a compound of somewhat complicated composition containing more than three molecules of lime. This view was afterwards opposed by Wibel, who, believing that there were no grounds whatever for Aeby's supposition, maintained that bone-phosphate was nothing more than a mixture of tricalcic phosphate and calcic carbonate. The author of this paper now describes experiments to prove that there is not even sufficient lime present to justify Wibel's conclusion, but that the phosphoric acid must partly exist as dibasic phosphate.

The bones of a dog were used for the experiments. Besides the phosphoric acid, lime, &c., the carbonic acid was determined both in

the raw bone and in the ash, and the difference between the results was added to the amount contained in the latter. On deducting from the total amount of lime that required for the saturation of the carbonic acid, and combining the remainder with phosphoric acid to form tricalcic phosphate, there remained an excess of phosphoric acid unaccounted for. The following example may serve to illustrate this:—

A sample contained in 100 parts 6.10 carbonic acid, 52.51 lime, 0.83 magnesia, and 39.74 phosphoric acid, the difference 0.82 corresponding to 1.42 per cent. fluorine.

6.10 per cent. carbonic acid requires 7.76 per cent. lime for the formation of calcium carbonate.

0.83 per cent. magnesia requires 0.98 per cent. phosphoric acid for the formation of magnesian phosphate.

1.42 per cent. fluorine requires 1.49 per cent. calcium for the formation of calcium fluoride.

There is left 42.66 per cent. lime and 38.76 per cent. phosphoric acid, and as 42.66 parts of lime require only 36.06 parts of phosphoric acid for the formation of tricalcic phosphate, there remains 2.70 per cent. phosphoric acid in excess.

This excess of phosphoric acid was found in every experiment, and the author explains it by supposing the bone phosphate to be partly bibasic and partly tribasic.

H. H. B. S.

Urea in the Blood. By P. PICARD (*Compt. rend.*, lxxxiii, 1179).

—Arterial and venous blood were extracted at the same moment from a healthy dog, the quantities were weighed, and the urea determined in them. It was found that the arterial blood contained a larger quantity of substance decomposed by Millon's reagent than venous blood, this difference disappearing entirely after exposure to the air for 15 or 20 minutes.

1000 grams of arterial blood contained 1.45 gram.

1000 grams of venous blood contained 0.80 gram.

A specimen of arterial blood gave 0.8 gram in 1000 grams when the estimation was made immediately, and 0.6 gram after one hour.

These figures show that there is a destruction in the blood of part of the substance found by Millon's reagent. It is also found that the numbers remain the same after the first destruction, and that if arterial and venous blood are both allowed to stand, and then the urea determined, the numbers obtained are nearly equal.

From these figures the author infers that there are two different substances in arterial blood, both decomposed by Millon's reagent; the one is eminently destructible, and disappears almost completely in the capillaries; the other, on the contrary, is stable, and exists in the same quantity in both arterial and venous blood. The first has not yet been studied; the second is probably urea.

C. W. W.

Chemical Character of the Pigment of the Negro Skin. By F. P. FLOYD (*Chem. News*, xxxiv, 179).—The cuticle from various negro subjects, after being carefully washed with water, alcohol, and ether, was ignited, and after weighing the ash, the iron therein was

determined. The percentage of ash averaged 2.40, which is nearly double that contained in the cuticle of the white man; the iron amounted to 2.28 per cent. of the ash, also nearly twice the quantity in the white man's cuticle. The presence of a considerable quantity of iron in the black pigment is therefore most probable, as is also the supposition that this pigment is a product of the alteration of the colouring-matter of the blood.

The brown or black pigment appears, from the author's experiments, to originate in the outer layer of true skin, its production being probably connected with loss of vitality of the cells, and to accompany these cells all the way to the surface. The author suggests that the chemical modification of the red blood-corpuscles may be dependent on feebleness of circulation in the superficial capillaries, the facts concerning diseases to which negroes are specially liable being in keeping with this supposition.

M. M. P. M.

Phenol-forming Substance in Human Urine. By E. SAL-KOWSKI (*Deut. Chem. Ges. Ber.*, ix, 1595—1597).—In a case of peritonitis, accompanied during life by obstruction of the bowels, the urine was tested for indican by means of hydrochloric acid and bleaching powder, which showed that a large quantity was presented, and at the same time the smell of chlorophenol was observed. On distilling the urine alone or with acetic acid, no phenol volatilised; but on distilling with hydrochloric acid, a distillate was obtained, in which bromine-water produced an abundant precipitate, varying during eight days from 0.2425 to 1.5575 grams per litre, while according to J. Munk, normal urine gives only about 0.004. When during the illness the quantity of indican diminished, that of the phenol decreased also, and *vice versa*. That the phenol-forming substance is phenyl-sulphuric acid appears probable, as, after treatment with hydrochloric acid, the quantity of sulphuric acid was increased. The precipitate produced by bromine is possibly not entirely due to phenol, but perhaps also to pyrocatechin, which, according to Baumann's researches, might be present in urine containing indican.

On injecting indol into a rabbit whose urine contained only traces of indican and phenol, these compounds soon made their appearance, but disappeared almost entirely when the injections were discontinued.

C. S.

Guanine in Pig's Urine. By DOMENICO PECILE (*Liebig's Annalen*, clxxxiii, 141—144).—The author has analysed the urine of a pig fed exclusively on bran, and in an unhealthy condition. The urine was of a bright yellow colour, slightly turbid, and had at first a faint acid reaction, but quickly became strongly alkaline, and deposited a bulky sediment. Its sp. gr. was 1.024 at 18°. The inorganic matters in 100 c.c. of the urine were as follows:—

Sodium chloride.....	0.106 gram.
" sulphate.....	0.113 "
Calcium phosphate, $\text{CaH}_2(\text{PO}_4)_2$	0.096 "
Magnesium phosphate, $\text{MgH}_2(\text{PO}_4)_2$..	0.177 "

Sodium phosphate, NaH_2PO_4	0.568 gram.
Potassium phosphate, KH_2PO_4	0.310 „
Phosphoric acid, H_3PO_4	0.355 „

The urine was found to contain also 19.98 grams of urea, 0.0034 gram of xanthine, and 0.0068 gram of *guanine* per liter. It was free from uric acid, and contained traces only of creatinine. The author thinks it possible that *guanine* is a constant constituent of the urine of even healthy animals. He is experimenting on the subject.

J. R.

The Natural Poison of the Human Corpse. By A. MORIGGIA (*Gazz. chim. ital.*, vi, 319).—Another series of experiments has been made, supplementing those noticed in this Journal (1876, ii, 647); the following are the chief results obtained:—

1. The poison exists even eighty days after death, in the corpses of men who have died of different diseases, and have been buried during rather warm weather, and in a warm place. Putrefaction advanced to this point seems therefore to generate the poison in comparatively large quantities.

2. The chemical purification, performed at the proper time, furnishes a visceral extract, free from the poison.

3. The poison may be extracted by various methods; ether removes it both from an acid and from an alkaline solution. Amyl alcohol is to be recommended, but not ethyl alcohol.

4. If the alkaline visceral extract contains strychnine, pure ether and amyl alcohol separate a certain amount of this body, together with the natural poison.

5. In legal cases it is better not only to use the whole of the viscera for one experiment, but to add the brain to them.

F. D. B.

Spectroscopy of the Colouring Matters of Blood. By H. W. VOGEL (*Deut. Chem. Ges. Ber.*, ix, 1472—1473).—A reply to Gänge. C. S.

Chemistry of Vegetable Physiology and Agriculture.

Experiments on the Respiration of Plants. By L. RISCHAWI (*Landw. Versuchs.-Stat.*, xix, 321—340).—A series of experiments on the influence of light and heat upon the respiration of plants was carried out some time since by Wolkoff and Mayer. Their results showed that the intensity of respiration is to a certain degree proportional to the temperature, that most conducive to it being about 35°C ., a temperature considerably higher than that found to be the most favourable to the growth of the plant. These experiments were afterwards followed up by Mayer alone, who determined the “respiration-curve” for wheat at the period of germination, and onwards during the sub-

sequent growth of the plant. He employed for this purpose essentially the same method as that used in his earlier researches carried out in conjunction with Wolkoff, a description of which has already been given in this Journal (page 417, vol. i, 1876). This method was not, however, free from defects. In order to determine the respiration-curve for the whole period of the germination of an etiolated plant, it was necessary to employ fresh seedlings for every experiment, so that the plants had continually to be changed; and further, as the small capacity of the apparatus did not permit of the respiration-intensity of larger parts being determined by direct observation, it was only possible to estimate it in this case by considering the loss in weight of dried substance.

In the experiments described in this paper the plants were kept in the respiration-apparatus during the whole of their development, and the amount of carbonic acid gas produced every day was carefully determined. This was done by drawing a continuous stream of air, firstly through a U-tube filled with potash, then through the cylinder containing the plants, and lastly through a tube charged with 75 c.c. of baryta-water of known strength. Every 24 hours this tube was emptied and re-filled, provision being made for doing this without detaching any part of the apparatus. The baryta-solution was drawn off into a small stoppered bottle, in which it was allowed to settle, and when the barium carbonate had completely subsided, 25 c.c. of the clear liquid was removed by a pipette, and titrated with a $\frac{N}{10}$ solution of nitric acid. From the difference in the strength of the baryta-water before and after use, the quantity of carbonic acid gas given off during the 24 hours was calculated. The first experiments were made with wheat plants, and in connection with the respiration of carbonic acid gas, measurements of the stalks were regularly taken.

The following table shows the results of one of the experiments made in this manner:—

February.	CO ₂ in mil- ligrams.	Temp.	March.	CO ₂ in mil- ligrams.	Temp.
17	13.86	21° C.	1	49.50	21° C.
18	19.14	"	2	49.50	"
19	32.34	"	3	49.50	"
20	37.62	"	4	42.90	"
21	42.90	"	5	41.36	"
22	44.88	"	6	33.66	"
23	46.86	"	7	33.00	"
24	47.52	"	8	30.36	"
25	48.18	"	9	28.38	"
26	48.88	"	10	25.74	"
27	50.16	"	11	21.12	"
28	49.50	"	12	18.48	"
29	49.50	"	13	15.18	"

All other experiments made with wheat-plants gave similar results. The curve, therefore, rises rapidly at the commencement of germina-

tion, reaches its maximum height on the 11th day, remains for a few days quite steady, and then gradually falls again. These results agree with those obtained in quite a different way by Mayer, and on comparing them with the daily measurements of the plants, the same relation can be seen between the curves of respiration and growth as that observed by him, viz., that the former reaches its maximum after the latter.

Experiments were then made with *Vicia faba*, but the results were quite different from those obtained with wheat. One experiment was commenced on January 17th, and continued until February 5th, but throughout the whole time the carbonic acid fluctuated only between 19.14 mgrms. and 23.74 mgrms., and even these slight differences can be explained by the variations in the temperature. Other experiments gave the same results. Notwithstanding, therefore, the vigorous growth of the plant, the respiration of carbonic acid continues always the same from the very commencement of germination.

The effect of pure oxygen gas upon respiration was next tried. For this purpose the cylinder of the apparatus was filled with bean-seedlings, and air and oxygen gas alternately passed through it. The results show that the quantity of carbonic acid produced is precisely the same in either case. The following are the results of one of the experiments; the temperature ranged from 21°—23° C.:—

	CO ₂ in milligrams.
9.35 a.m. after 1 hour in atmospheric air	26.40
10.40 " " in oxygen gas	24.42
11.45 " " in atmospheric air	24.42
12.50 p.m. " in oxygen gas	23.76
1.55 " " in atmospheric air	24.42
3.0 " " in oxygen gas	25.65

Numerous other experiments gave all similar results.

The following are the results of some experiments on the influence of temperature on respiration:—

23 bean-seedlings were placed in the apparatus. Temperature, 20° C.

During 1 hour in atmospheric air.....	39.60 mgrms. CO ₂ .
" " in oxygen gas	39.60 "

The temperature was gradually reduced to 6° C.

During 1 hour in atmospheric air.....	21.22 mgrms. CO ₂ .
" " in oxygen gas	21.22 "

The temperature was further reduced to 2° C.

During 1 hour in atmospheric air.....	10.56 mgrms. CO ₂ .
" " in oxygen gas	10.56 "
" " in atmospheric air.....	10.56 "
" " in oxygen gas	9.90 "

The temperature was then gradually raised to 18° C.

During 1 hour in atmospheric air.....	32.34 mgrms. CO ₂ .
" " in oxygen gas	31.68 "

These experiments show that an increased supply of oxygen gas has no influence upon the respiration of carbonic acid, either at the lower or higher temperature, and this was also found to be true for temperatures of 30° and 35°.

H. H. B. S.

On the Dependence of Plant Respiration upon Temperature. By ADOLF MAYER (*Landw. Versuchs.-Stat.*, xix, 340—349).—Experiments were made with *Triticum vulgare*, with the object of determining the "respiration-curve" of a germinating plant at increasing temperatures. Wolkoff and Mayer's respiration-apparatus was used, the quantity of oxygen consumed by the plants being taken as the measure of respiration.

The results show that respiration commences at temperatures much lower than the minimum required for growth, even in fact below 0° C., and that it rises proportional to the temperature far above the maximum of growth, ceasing only with the life of the plant. These experiments therefore prove the truth of the conclusions deduced indirectly from the results of the author's former researches. (*Landw. Versuchs.-Stat.*, xviii, 277; *Journ. Chem. Soc.*, 1876, vol. i, p. 419).

H. H. B. S.

Action of Carbonic Oxide on Plants. By A. STUTZER (*Deut. Chem. Ges. Ber.*, ix, 1570—1571).—Young and well-formed plants of *Brassica* and *Triticum* were exposed to an atmosphere of carbonic oxide, but after a lapse of 30—40 days, no new leaves appeared. Atmospheric air, freed from carbonic anhydride, and mixed with 3—4 per cent. of carbonic oxide, also failed to promote vegetation. Other experiments with a mixture of CO + H₂ also gave negative results. Hence it would seem that chlorophyll has not the power, as Baeyer suggested, of combining directly with carbonic oxide, but probably a direct conversion of carbonic anhydride into carbohydrates takes place in the cells containing chlorophyll.

G. T. A.

Composition of Leaves. By P. FLICHE and L. GRANDJEAN (*Ann. Chim. Phys.* [5], viii, 486—511).—The leaves of four trees, the acacia (*Robinia pseudo-acacia*), the wild cherry (*Uerasus avium*), the chestnut (*Castanea vulgaris*), and the birch (*Betula alba*), all of which grew on a chalky soil, were collected at different times of the year and examined microscopically and chemically.

The chlorophyll was found in the spring leaves already in considerable abundance; it remained in full quantity during the summer, and in the autumn was completely destroyed and replaced by a brown substance.

The starch underwent analogous changes, but it did not form so early and was in no case entirely destroyed.

The following table gives the composition of the fresh leaves :—

Species.	Date of collection.	Water p.c.	Ash referred to the fresh substance.	Nitrogen.	Ash referred to dry substance.
I. Acacia.....	May 2	73.5	2.33	3.59	6.25
II. id.	July 3	64.1	2.76	2.81	7.75
III. id.	Sept. 7	55.7	4.15	1.68	8.22
IV. id.	Oct. 13	55.4	5.16	0.70	11.74
V. Cherry	April 28	70.0	2.32	2.00	7.80
VI. id.	July 3	60.23	2.77	0.95	7.30
VII. id.	Sept. 7	54.4	2.89	0.84	6.39
VIII. id.	Oct. 2	54.2	3.28	0.11	7.24
IX. Birch	April 30	67.5	1.24	2.51	3.84
X. id.	Sept. 14	54.0	1.95	1.28	4.30
XI. id.	Oct. 9-15	50.25	2.28	0.49	4.68
XII. Chestnut ..	May 1	72.0	1.28	2.12	4.60
XIII. id.	Sept. 16	57.0	2.00	0.70	4.75
XIV. id.	Oct. 12	44.8	2.38	0.62	4.55

The ash of the leaves was also submitted to analysis, the results of which are given in the following table:—

Species.	H ₃ PO ₄	CaO.	MgO.	K ₂ O.	Na ₂ O.	Fe ₂ O ₃	Mn ₂ O ₃	SiO ₂	H ₂ SO ₄	Cl.	CO ₂
I. Acacia	21.16	20.82	9.67	30.60	6.37	0.91	trace.	3.72	7.89	trace.	5.08
II. id.	8.69	48.64	11.02	19.20	5.71	1.43	id.	1.67	3.63	id.	21.62
III. id.	5.31	72.97	5.50	6.62	3.91	1.21	id.	2.05	2.42	id.	31.65
IV. id.	1.90	72.00	6.16	3.25	1.34	1.46	10.64	1.68	2.13	id.	28.30
V. Cherry.....	15.80	30.57	7.82	32.78	1.89	0.95	4.42	1.41	1.34	id.	17.60
VI. id.	8.20	38.06	18.38	17.80	6.44	1.29	5.62	1.76	2.46	id.	20.07
VII. id.	5.93	44.70	14.29	12.15	9.33	1.17	7.39	2.72	1.86	id.	20.48
VIII. id.	3.81	44.05	17.79	11.82	5.00	1.19	13.25	2.30	0.79	id.	23.88
IX. Birch	17.46	28.72	4.40	25.54	0.43	0.72	15.87	1.73	5.19	id.	7.92
X. id.	10.99	40.03	11.68	7.22	1.89	1.20	21.48	2.75	2.75	id.	16.90
XI. id.	8.63	50.76	16.41	2.88	4.57	1.18	9.81	2.54	3.21	id.	18.20
XII. Chestnut..	19.31	18.41	9.16	31.85	2.39	0.50	11.84	1.59	4.98	id.	7.34
XIII. id.	9.22	39.06	7.11	16.95	5.31	1.33	16.64	1.95	2.42	id.	10.05
XIV. id.	8.35	49.50	6.90	10.52	2.59	2.17	12.52	4.67	2.75	id.	13.22

From these numbers and from other considerations, the authors deduce the following general laws:—

1. From the time of the bursting of the buds to their fall, the leaves of trees accumulate dry matter.

2. They lose a part of their nitrogen, which is reabsorbed, while the proportion of ash increases.

3. The proportion of phosphoric acid, sulphuric acid, and potash diminishes in the ash.

4. That of the lime, iron and silica increases.

5. No law can be established for the magnesia, soda, and manganese.

6. The leaves of trees of different species require for their constitution nearly equal quantities of water.

7. They require unequal quantities of nitrogen and of ash.

8. The proportions of the different elements in the ash varies in different species.

9. It follows from the last three propositions that some trees take much more from the soil than others.

10. Dead leaves do not make a good manure; nevertheless their removal is very deleterious to forests. C. W. W.

Presence of Sugar in the Leaves of Beets. By CORENWINDER (*Compt. rend.*, lxxxiii, 1238).—The ribs contain the principal part of the sugar in the leaves; 100 c.c. of the juice from these ribs contained 2·086 grams of glucose, and the ribs themselves contained 1·607 per cent. of glucose. The leaves contain also a small quantity of crystallisable sugar. It was found that beets having large leaves contained a larger percentage of sugar than those with small leaves.

C. W. W.

Silica in Grasses. By P. B. WILSON (*Am. J. of Sci.* [3], xi, 373—375).—In the straw of wheat grown on land to which infusorial earth containing diatomaceæ had been applied, the author found the siliceous shield sharply and distinctly defined in their original forms as they occur in the infusorial earth, except that the larger discs (*Actinocyclus*, *Ehrenbergii*, and *Actinoptychus undulatus*) were absent in their perfect condition. The author infers that plants take up silica only when it is present in a state of fine subdivision, and that the application of silicates as fertilizers is useless, since we have no reason to believe that plants have the power of separating silica from its combinations. R. R.

Analyses of Roots of Filix Mas. By KRUSE (*Arch. Pharm.* [3], ix, 24—32.)—The roots were gathered in the neighbourhood of Wolmar during April, July, and October, 1874.

Dried at 100°.	April.	July.	October roots.
Moisture	15·7	13·4	13·5 p.c.
Ash of roots dried at 100°..	2·2	2·5	2·5 "
Aqueous extract	36·4	25·4	35·8 "
Alcoholic do.	27·3	26·1	39·5 "
Ethereal do.	10·3	12·4	11·5 "
Petroleum spirit extract ..	9·3	8·4	9·1 "
Amylose	28·2	22·7	15·4 "
Tannic acid by precipitation with copper acetate	4·6	6·9	5·9 "
Tannic acid by precipitation with lead acetate	9·2	9·8	11·7 "
Filix-red	5·2	6·9	7·8 "
Gum and albumin.....	5·5	2·3	2·1 "

Filicic acid could not be estimated.

M. M. P. M.

Chemical Examination of Füh-ling (*Lycoperdon solidum*) from China. By J. L. KELLER (*Chem. News*, xxxiv, 168).—This substance occurs in China, Japan, and several American States. That from China was described in *Hanbury's Chinese Materia Medica*. It is described as resembling a round tuber, with a rough black exterior, growing on the roots of fir-trees, and supposed to be a disease of the root caused by a fungus. The white internal substance is slightly soluble in alcohol and in water, and the solution yields a flocculent precipitate with lead acetate. It dissolves more freely in sodium carbonate, and gives with acids a precipitate of pectic acid.

In America it is called "tuckahoe," or Indian bread. A sample described in the *Report of the United States Department of Agriculture* has the following composition:—Nitrogenous matter, 4.09; ash, 1.61; starch, 81.80; water, 12.50. Dr. John Terry investigated it, and stated that it is composed of a substance called *sclerotin*, which was subsequently called pectin by Braconnot. R. T. Brown, chemist of this department, gives the following analysis:—Moisture, 14.16; glucose, 0.93; gum, 2.60; pectose, 17.34; nitrogen, in an insoluble form, 0.36; woody fibre, 64.45; ash, 0.16 = 100.

As all the specimens of Füh-ling subjected to analysis, were of American origin, the author has analysed a specimen from China.

Sol. in water, = 4.63 per cent.	{	Glucose	0.87
		Gum, with a trace of acid	2.98
		Albuminoid matter (calculated from nitrogen)	0.78
Insol. in water, 81.03	{	Pectose (estimated by difference)	77.27
		Cellulose (insoluble in sodium hydrate)	3.76
		Mineral matter, soluble in water	0.08
		insoluble	3.56
		Water	10.70
			100.00

Analysis of ash from 100 grams.

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	Cl.	SiO ₂ .
4.675	2.192	5.109	11.375	11.808	19.781	1.587	1.643	41.771 = 100

The crude ash contained 2.813 per cent. of carbonic anhydride, 2.209 of charcoal, and 50.546 of sand. The sand is probably derived from the soil being forced into the plant by the growth of the fungus.

W. R.

Composition of Eatable Mushrooms. By A. v. LÖSECKE-HILDBURGHAUSEN (*Arch. Pharm.* [3], ix, 133—146).

	Calculated on fresh substance.					
	Water.	Protein.	Ash.	Fat.	Carbohydrates and extractive.	Fibre.
1. <i>Fistulina hepatica</i>	85·00	1·59	0·94	0·12	11·40	1·95
2. <i>Clavaria botytis</i>	89·35	1·21	0·66	0·29	7·66	0·73
3. <i>Polyporus ovium</i>	91·00	1·20	0·21	0·86	4·73	2·00
4. <i>Boletus granulatus</i>	88·50	1·61	0·75	0·23	7·49	0·82
5. <i>Agaricus melleus</i>	86·00	2·27	1·05	0·73	9·14	0·81
6. <i>Boletus bovinus</i>	91·34	1·49	0·52	0·41	5·52	0·72
7. <i>Agaricus matubilis</i>	92·18	1·40	0·46	0·17	4·47	0·62
8. <i>Boletus elegans</i>	91·10	1·88	0·53	0·14	5·57	0·60
9. <i>Agaricus caporatus</i>	90·67	1·91	0·56	0·19	5·52	0·57
10. <i>Boletus luteus</i>	92·25	1·72	0·49	0·29	4·45	0·80
11. <i>Agaricus ulmarius</i>	84·67	4·02	1·94	0·49	7·93	0·95
12. Do. <i>procurus</i>	84·00	4·65	1·12	0·57	8·55	1·11
13. Do. <i>oreades</i>	91·75	2·93	0·87	0·19	3·59	0·67
14. Do. <i>primulus</i>	89·25	4·11	1·61	0·14	4·08	0·81
15. Do. <i>excoriatus</i> ..	91·25	2·69	0·83	0·45	4·41	0·82
16. <i>Lycoperdon bovista</i> ..	86·92	6·62	1·20	0·41	3·42	1·43
17. <i>Boletus edulis</i>	—	—	—	—	—	—
18. <i>Cantharellis cibarius</i> ..	—	—	—	—	—	—
19. <i>Clavaria flava</i>	—	—	—	—	—	—
20. <i>Morchella esculenta</i> ...	—	—	—	—	—	—
21. <i>Tuberclarium</i>	—	—	—	—	—	—
22. <i>Morchella conica</i>	—	—	—	—	—	—
23. <i>Helvella esculenta</i>	—	—	—	—	—	—
24. <i>Agaricus campestris</i> ..	—	—	—	—	—	—
25. Veal.....	62·30	16·60	4·48	16·60	—	—
26. Beef.....	54·00	17·80	5·56	22·60	—	—
27. Lentils.....	14·50	23·80	3·00	2·60	52·00	6·9
28. Pease.....	14·30	22·40	2·50	2·50	51·60	9·20
29. Rye meal.....	14·00	10·50	1·60	1·60	70·80	1·50
30. Wheat do.	12·60	11·00	0·70	1·20	73·00	0·70
31. Various cabbages	80·00	2·28	—	0·12	2·14	0·93
	to	to		to	to	to
	93·00	5·63		0·17	11·24	1·81
32. Various turnips	81·00	1·00	0·7	0·10	8·40	1·0
	to	to	to	to	to	to
	92·00	1·60	1·0	0·20	15·40	1·70

	Calculated on dry substance.				
	Protein.	Ash.	Fat.	Carbohy- drates and extractive.	Fibre.
1. <i>Fistulina hepatica</i>	10·60	6·33	0·81	69·26	13·00
2. <i>Clavaria botrytis</i>	12·32	6·23	2·80	71·80	6·85
3. <i>Polyporus ovium</i>	13·34	2·33	9·60	52·51	22·22
4. <i>Boletus granulatus</i>	14·02	6·42	2·04	70·39	7·13
5. <i>Agaricus melleus</i>	16·26	7·50	5·21	65·25	5·78
6. <i>Boletus bovinus</i>	17·24	6·00	4·80	63·65	8·31
7. <i>Agaricus matabilis</i>	19·73	6·46	2·40	62·71	8·70
8. <i>Boletus elegans</i>	21·21	6·00	1·60	64·45	6·74
9. <i>Agaricus caporatus</i>	20·53	6·02	2·11	59·02	12·32
10. <i>Boletus luteus</i>	22·24	6·39	3·80	57·25	10·32
11. <i>Agaricus ulmarius</i>	26·26	12·65	3·20	51·63	6·26
12. Do. <i>procureus</i>	29·08	7·00	3·60	53·39	6·93
13. Do. <i>orcadus</i>	35·57	10·57	2·40	43·34	8·12
14. Do. <i>primulus</i>	38·32	15·00	1·38	37·77	7·53
15. Do. <i>excoriatus</i>	30·79	4·34	5·14	50·36	9·37
16. <i>Lycoperdon bovista</i>	50·64	9·18	3·20	26·05	10·93
17. <i>Boletus edulis</i>	22·82	6·22	1·98	62·43	6·55
18. <i>Cantharellus cibarius</i>	23·43	8·19	1·38	57·53	9·47
19. <i>Clavaria flava</i>	24·43	9·75	2·13	56·75	6·94
20. <i>Morchella esculenta</i>	33·90	9·74	1·71	48·07	6·58
21. <i>Tuberclarium</i>	36·32	9·73	2·48	23·00	28·31
22. <i>Morchella conica</i>	36·25	8·97	1·52	44·11	6·20
23. <i>Helvella esculenta</i>	26·31	—	2·25	53·52	6·89
24. <i>Agaricus campestris</i>	20·63	5·80	—	—	—
25. Veal	44·03	—	—	—	—
26. Beef	38·70	—	—	—	—
27. Lentils	27·83	—	—	—	—
28. Pease	26·13	—	—	—	—
29. Rye meal	12·20	1·86	1·86	82·32	1·74
30. Wheat do.	13·62	0·80	1·37	38·52	0·80
31. Various cabbages	{ 14·9 to 36·9 5·4	{ —	{ 1·5 to 5·4	{ 30·2 to 53·3	{ 9·2 to 19·3
32. Various turnips	{ to 12·3	{ —	{ —	{ —	{ —

These analyses show the relative nourishing power of the various mushrooms as compared with other good materials. M. M. P. M.

Analytical Chemistry.

Disintegration of Silicates. By C. STÖCKMANN (*Zeitschr. Anal. Chem.* 1876, 283—285).—The difficulty sometimes experienced in removing the fused mass of silicates from the crucible may be overcome, and the objectionable practice of suddenly cooling the crucible and its contents discontinued, if the whole be allowed to cool gradually and then slightly heated sufficiently to melt the rim of the cake. Upon cooling the cake is easily removed, or it may be covered with water and slightly heated, when it immediately loosens. F. J. L.

Application of the Ferrosopyrogallie Reagent to the Estimation of Bicarbonates in Waters. By E. JACQUEMIN (*J. Pharm. Chim.* [4], xxiii, 412—419).—The reagent is prepared by mixing equal volumes of solution of pyrogallie acid, 5 grams per litre, with solution of ferric chloride, 2 grams per litre. The liquid gradually becomes turbid by the deposition of purpurogallin, but this may be removed by filtration, and the preparation will thus be available for use for a fortnight. About 10 c.c. may be mixed with 250 c.c. of the water to be analysed, and the normal acid added from a graduated pipette. The presence of bicarbonates is indicated by an intense blue-violet colour, ammoniacal salts being absent, for they also impart the like colour. When the decomposition of the bicarbonates is nearly complete, the blue colour becomes feebler, and the termination of the reaction is marked by an abrupt change of tint to light-brown. R. R.

Quantitative Estimation of Metals by Electrolysis. By F. WRIGHTSON (*Zeitschr. Anal. Chem.*, 1876, 297—306).—Portions of normal solutions of the metals, after addition of nitric acid or ammonia, were diluted with water to 200 c.c., and then precipitated on platinum by a current from a thermopile. The strength of the current was such as to yield, by the decomposition of water, 100 c.c. of mixed gases in an hour.

The results obtained are as follows:—

a. *Copper*.—The metal is completely precipitated, but in order to get correct results, the current must not be stopped whilst the metal is in contact with the acid. To obviate this, the liquid should be syphoned off and the metals well washed with water at the same time.

b. *Copper and Antimony*.—More or less antimony was always precipitated together with the copper.

c. *Nickel and Copper*.—Pure ammoniacal solutions of nickel gave good results. In a mixture of nickel and copper dissolved in nitric acid, the copper was nearly precipitated, 1.189 per cent. being found instead of 1.2055 per cent. (This result is vitiated by the presence of ammonium chloride.) The solution is then strongly concentrated, sulphuric acid added, and the whole evaporated until no nitric acid remains. Ammonia is now added to the residue, the whole made up

to 200 c.c., and the nickel precipitated, 1.868 per cent. being found instead of 1.885 per cent.

d. *Cadmium*.—No practical result.

e. *Zinc*.—No practical result.

f. *Cobalt*.—This may be estimated in exactly the same manner as nickel, and gives good results.

g. *Nickel and Cobalt*.—One experiment only was tried, which gave no result.

h. *Copper and Nickel in a Smelting Product*.—Three estimations of copper gave 26.29 per cent., 26.35 per cent., and 26.20 per cent. respectively. Only one estimation of nickel was made.

i. *Nickel and Iron*.—Both metals are completely separated simultaneously.

F. J. L.

Fluorescëin as an Indicator in Titration.—By F. KRÜGER (*Deut. Chem. Ges. Ber.*, ix, 1572).—Fluorescëin loses its fluorescence in presence of the slightest trace of an acid, and regains it immediately on addition of an alkali. The appearance and disappearance of the fluorescence is more marked in coloured solutions (if the colour is not too deep) than in colourless liquids. The action is not prevented by carbon dioxide, but it is inapplicable in presence of free acetic acid, which itself dissolves fluorescëin with fluorescence. Fine white precipitates, such as barium sulphate, mask the appearance of the fluorescence, and must be allowed to settle before the reaction can be determined.

G. T. A.

Detection of Free Sulphur. By MAX ROSENFELD (*Zeitschr. Anal. Chem.*, 1876, 294).—A small quantity of the substance to be tested having been finely ground is spread out over the inner surface of a funnel, and then brought in contact with a hydrogen flame. If sulphur is present the flame is coloured blue. In a note to this paper Fresenius states that selenium and tellurium treated in a similar manner give respectively a light blue and greenish-blue coloration to the flame, and consequently somewhat interfere with the detection of sulphur in their presence.

F. J. L.

Estimation of Potassium as Acid Tartrate. By P. CASAMAJOR (*Chem. News*, xxxiv, 242—245).—In order to find the quantity of potassium in a compound it is in the first place necessary to add a large quantity of tartaric acid, not more, however, than three times as much as the quantity of material weighed for analysis. 10 c.c. of decinormal solution contain 47 centigrams of potash (equivalent to 39 centigrams of potassium), and require about 2 grams of tartaric acid. The liquid, after the addition of this acid, is stirred sufficiently to make a thorough mixture of the solutions, when the crystals begin to deposit almost immediately. Alcohol should be added as soon as the liquid becomes clear. It is best to add at first only a small quantity—equal in volume to about one-tenth of the liquid in the beaker. After stirring and leaving the mixture at rest for five minutes, the whole of the alcohol is added, in quantity sufficient to make the whole liquid in the beaker contain at least 60 per cent. of alcohol in volume. After the

deposition of crystals has stopped, the contents of the beaker are quickly thrown on a filter, and the residue on the filter is washed with alcohol of 60 per cent. until the filtered liquid ceases to show a red colour with litmus. The precipitate after this is ready to be washed down into a beaker, and the cream of tartar in water placed under a burette. If the operation has been carefully conducted, it will take exactly 10 c.c. of the decinormal potash solution to turn the liquid from red to blue.

The condition of a solution containing only potash and water is a very rare one in chemical analysis. Regarding compounds with potassium, it was found that by exactly neutralising 10 c.c. of a decinormal solution with sulphuric acid, and then adding 2 grams of tartaric acid as before, a very slight precipitate will be obtained, even after standing for hours, or whatever quantity of alcohol may be added. If, instead of stopping at neutrality, an excess of acid is added, tartaric acid does not produce the least turbidity. Hydrochloric, hydrobromic, hydriodic, nitric, and phosphoric acids behave in the same manner as sulphuric acid. These acids are strong mineral acids, whose affinities for potassium are so great that although the acid tartrate is less soluble than any of their potassic compounds, they yield only a small portion of potassium to tartaric acid. If, therefore, a weaker acid than tartaric acid was chosen to combine with potassium, it would not prevent the production of an abundant deposit of acid tartrate. Acetic acid was found incapable of preventing this precipitation.

Salts of sodium in a solution containing 60 per cent. of alcohol do not prevent the precipitation of cream of tartar. The sulphate, nitrate, chloride, iodide, bromide, tartrate, and acetate seem equally powerless to prevent the formation of the precipitate. This is an important fact, showing that it is possible by means of soda or its carbonate to separate the fixed bases accompanying potassium, and likewise ammonia, which forms a very sparingly soluble tartrate, and may, in presence of soda, be driven off by heat.

Instead of the addition of acetic acid, as above suggested, it is better to add acetate of sodium, which, if a strong mineral acid is present in excess, forms a sodium salt by acting on the acetate, and liberates a corresponding quantity of acetic acid. When tartaric acid is afterwards added, and a quantity of acid tartrate is precipitated, the strong mineral acids set free react on the acetate, and acetic acid is again liberated. This action goes on until all the potassium has been precipitated as acid tartrate, and all the strong mineral acids originally combined with potassium have been combined with sodium, and a corresponding quantity of acetic acid has been set free. The quantity of sodium acetate used is equal to the quantity of tartaric acid.

The process above described is not always advisable, as the strength of the alcohol may in some cases interfere with the results.

In testing the low products of sugar-houses for potassium, strong alcohol cannot be used, because they contain substances which become adhesive and unmanageable in presence of strong alcohol. By adding sufficient tartaric acid to 10 c.c. of titrated potash solution in a beaker, to precipitate the potassium, a certain portion will be

deposited, but another part, although converted into cream of tartar, will remain in solution. If the precipitate is thrown on a filter without the addition of alcohol, and freed from tartaric acid by washing with water, a further loss will take place. If instead of using pure water to dissolve the tartaric acid and wash the precipitate, we use a liquid incapable of dissolving cream of tartar, the loss will be very much reduced. This can easily be done by using a saturated solution of acid tartrate, and washing the last portion of this solution on the filter with a small quantity of alcohol of 60 per cent. There will then remain one cause of error, due to the water introduced with the 10 c.c. of titrated potash solution, which may with sufficient approximation be considered as 10 c.c. of water. To estimate the quantity, Chancel's table must be used, and by supposing that the temperature of the liquid is 25°, it will be found that, at that temperature, 100 c.c. of water will dissolve 67 centigrams of acid tartrate, and therefore 10 c.c. will dissolve 67 milligrams, equivalent to $16\frac{1}{2}$ milligrams of potash, and consequently to 0.35 of 1 c.c. of decinormal solution. If we have operated with care we shall find that we can account for the original 10 c.c. of potash solution within one-tenth of a c.c. The results, however, are not nearly so accurate when salts of sodium are present, and there is always a deficiency of acid tartrate precipitated. A small quantity of alcohol was found to overcome this difficulty, but by using too much alcohol, as much as 10 per cent., the results are too high. 3 per cent. has been adopted as the strength of the alcohol that gives the best results, and as the quantities of acid tartrate dissolved by 3 per cent. alcohol varies with the temperature, the author was led to make out the following table, giving grams of cream of tartar dissolved at a certain temperature in 100 c.c. of water with 3 per cent. of alcohol:—

0° = 0.21	15° = 0.37	30° = 0.60
5° = 0.25	20° = 0.45	35° = 0.75
10° = 0.32	25° = 0.54	40° = 0.84

D. B.

On a Quick Method of Estimating Lime in Presence of Magnesia, and on the Application of Magnesia to the Defecation of Sugar-liquors. By C. BERNARD and L. EHRMANN (*Compt. rend.*, lxxxiii, 1239).—In consequence of the insolubility of magnesia in solutions of sugar, it can easily be separated from lime by precipitation as hydrate in a solution containing sugar, and the lime may be estimated in the filtrate. Both substances may then be weighed as anhydrous oxides.

It was found that with 3 to 5 grams of magnesia per litre of juice, the defecation was nearly complete, and the juice filtered with great facility. By using magnesia instead of lime, a yield was obtained of 6 or 7 per cent. more than usual. The quality of the sugar was also greatly improved.

The magnesia was used as hydrate, carbonate, and phosphate, but the hydrate was found to be preferable. By the use of magnesia the necessity for employing carbonic acid to throw down the excess is

obviated, since the magnesia does not form a sucrate, and any excess of it that may be added remains in the scum. C. W. W.

Precipitation of Iron and Alumina by Sodium Acetate. By M. JUNGCK (*Zeitschr. Anal. Chem.*, 291).—All difficulty in the washing of this precipitate may be prevented by neutralising the liquid before precipitation, diluting with warm water, and then adding a large excess of sodium acetate. The resulting precipitate rapidly subsides after boiling, consists of large flocks, and may be easily washed. F. J. L.

Method for detecting the Adulteration of Lead Iodide. By L. ALESSANDRI and C. CONTI (*Gazzetta chimica italiana*, vi, 322). Several mixtures were made, similar in appearance to lead iodide, with those substances which are most easily employed in the falsification of that article, such as chromate and carbonate of lead, barium sulphate, &c. These mixtures were then submitted to the action of various reagents, from which potash and ammonia were selected, since with these the presence of chromate is most easily detected. A portion of the mixture containing chromate is heated with a little potash in solution, when it becomes reddish, owing to the formation of barium chromate; if a little more potash be added and the mass warmed, a yellowish liquid is obtained, with or without solid residue, according as barium sulphate was or was not originally present.

The whole method of procedure is given; the several tests would take as much time as a complete analysis of the substance.

F. D. B.

On Phosphorus as a Test for Iodates. By POLLACCI (*J. Pharm. Chim.* [4], xxiii, 178—180). Corne ascribes the reduction of iodates by phosphorus to the acids of phosphorus which are formed. The author proved by experiment that these acids are without action, and that the virtual reducing agent is the phosphorus itself, which, even in the amorphous state, acts so violently as sometimes to produce an explosion. W. R.

Method of Testing for Impurities in Potassium Iodide. By LEPAGE (*J. Pharm. Chim.* [4], xxiii, 261—263). The novelty of this method consists in dissolving out all potassium iodide from the commercial sample with 90 per cent. alcohol, and testing for the impurities,—carbonate, iodate, sulphate, chloride, and bromide of potassium,—in the residue, by the ordinary processes. W. R.

New Test for Acids and Alkalis. By F. FRÉBAULT (*J. Chim. Pharm.* [4], xxiii, 263—264). The author uses potassium and sodium picramates, which have a bright red colour, and turn greenish-yellow when treated with the weakest acids. Filter-paper soaked in a solution of calcium picramate may be used for the same purpose, and may advantageously replace litmus. W. R.

Effect of Silicic Acid upon the Estimation of Phosphoric Acid by Ammonium Molybdate. By E. H. JENKINS (*Am. J. of Sci.*

[3], xi, 204—206). The author's experiments show that the presence of silicic acid does not interfere with phosphoric acid estimations by the molybdic method. M. M. P. M.

Zinc for Analytical Use. By R. D. BOHANNON (*Chem. News*, xxxiv, 190). Zinc which is to be used for reducing ferric salts in the volumetric estimation of iron by permanganate, must be free from iron and carbon. The author precipitates a solution of commercial zinc in hydrochloric acid with sulphuretted hydrogen, filters, oxidises iron, and precipitates with ammonia, a little zinc also coming down, separates the filtrate and throws the zinc chloride, mixed with sodium and diluted with sodium chloride or zinc oxide, into a clean, hot earthen crucible. The sodium must be quite free from adhering naphtha. An excess of zinc chloride must be employed. M. M. P. M.

Recovery of Uranium Residues. By A. GAWALOVSKI (*Zeitschr. Anal. Chem.*, 1876, 292—294). The uranium phosphate, having been collected upon a filter, is washed once or twice so as to separate the greater portion of the soluble salts; it is then added to a saturated solution of ammonium carbonate, in which it dissolves, any portion that remains undissolved soon disappearing upon the addition of a slight excess of ammonium carbonate or on slightly warming. Should a sediment remain the liquid is filtered. To the clear solution ammonia is now added in excess, and then magnesia mixture, and the whole left for 10 or 12 hours, when the phosphoric acid will be precipitated and may be filtered off. The solution is evaporated to half its original bulk, hydrochloric acid added in excess, the whole brought to the boil so as to completely expel carbonic acid, and then ammonia free from carbonic acid added in excess. The precipitated uranium is filtered off, well washed, and may then be dissolved in hydrochloric or nitric acid for use.

The author is perfecting a similar method for the quantitative determination of uranium. F. J. L.

A New Reagent for the Detection and Estimation of Glucose. By A. SOLDANI (*Gazzetta chimica italiana*, vi, 322). The author, after reviewing rapidly the inconveniences presented by the reagents of Fehling and Barreswil, inconveniences not wholly removed even by the exhaustive work of Lagrange, passes to the description of the method of preparation and of the properties of his new reagent.

416 grams of potassium bicarbonate (best commercial), 15 grams of basic cupric carbonate (dry), and 1,400 grams of distilled water are heated together for about 6 hours on a sand-bath in a porcelain dish, the liquid being always maintained at the same level; the copper salt is attacked by the alkaline carbonate, carbonic anhydride is evolved, and the liquid becomes greenish; if the liquid is allowed to concentrate, the cupric carbonate dissolves rapidly, but is reprecipitated on addition of water. When the evolution of carbonic anhydride has nearly ceased, the liquid is made up to its original volume with water, the heat is then discontinued, and after standing and

filtering, the whole is concentrated down to 800 c.c. In winter this reagent often deposits crystals of potassic bicarbonate: this, however, is easily remedied by reducing it only to 1000 c.c. if it is for use in cold weather. It is not reduced by the action of light, or by the carbonic anhydride of the atmosphere. It is unaltered by prolonged boiling, and may be evaporated to dryness at a gentle heat, leaving a blue substance which is attacked by glucose.

No precipitation takes place on the addition of water, unless so much is added that the colour entirely disappears; the solution diluted with 15 times its volume of water remains unaltered in the cold, but is decomposed after long boiling, but without reduction; when diluted with three times its volume of water, it is unaltered by boiling. Finally, when a solution of bicarbonate of potash is coloured with a few drops of the reagent, the liquid may be boiled and even evaporated to dryness without decomposition.

The reduction by glucose is more easily carried out when the liquid is heated than when it is cold. In the latter case 20 times as much sugar is required to complete the reduction within 24 hours.

This reagent is as sensitive as Fehling's. It is not reduced by tartaric acid, but on boiling it with tannic acid, reduction is apparent. Uric acid forms a green precipitate of urate of copper; the same is the case with healthy urine, but if the latter contain glucose, reduction of the reagent takes place. The author, however, is not in a position to assert the possibility of distinguishing morbid urinal secretions by this means.

The reagent is reduced by formic acid, levulose, and lactose, but is unaltered by a solution of potato-starch; it would appear also that the purest saccharose and dextrin are without action upon it.

In order to test for glucose, it is not necessary to have the solution previously prepared; a crystal of potassium bicarbonate and a trace of cupric carbonate are dissolved in the liquid to be tested, which is then evaporated to dryness. If glucose is present, yellow spots will be observed; if not, the residue will be of a blue colour.

The reagent, to which the name of *potassic-cupro-bicarbonate* is given, may be used in quantitative analysis in the same manner as Fehling's test.

F. D. B.

Estimation of Alcohol by the Boiling Point. By M. SALLERON (*J. Pharm. Chim.* [4], xxiv, 33—35).—The author has studied Vidal's ebullioscope, as to the value of its indications of the amount of alcohol in wines and spirits. He finds that the solution of sugar, gum, tartrates, &c., in these liquids, lowers the boiling point, while acetic acid raises it. For these reasons, and because the indications of the instrument are liable to variations from changes of atmospheric pressure and other causes, he much prefers the process of estimation by distillation.

R. B.

Dr. E. Davy's Test for the Purity of Chloroform. By D. B. DORR (*Chem. News*, xxiv, 191).—The author holds that small quantities of alcohol cannot be regarded as an impurity in chloroform; further, that the volatile oils obtained in the purification of chloroform

do not give a blue colour with Davy's molybdic acid test, and that the production of this colour in chloroform points only to the presence of alcohol. M. M. P. M.

Anthracene Testing. By F. VERSMANN (*Chem. News*, xxxiv, 177, 191, 201).—The author's test is as follows:—Boil 1 gram of the sample for 4 hours with 15 grams of chromic acid dissolved in 10 c.c. of glacial acetic acid and 10 c.c. of water; allow the solution to stand for 12 hours; collect the crystals which form on a small filter, allowing the liquid to drain off completely; wash with boiling water until the filtrate is colourless; dilute to 600 c.c., and after 2 hours collect the powdery precipitate which has formed on a second filter, and wash well. Treat the crystals and powder with permanganate and potassium hydrate as in the usual test; collect each separately; dry and weigh. Take the melting and solidifying point of each. The crystals are to be considered as pure anthraquinone. Experiments are detailed which appear to show that the powder may be considered as anthraquinone if its melting and solidifying points lie between 270° and 280°, but as useless impurity if these points lie above or below those limits.

The two main conditions to be fulfilled in producing a pure anthracene are strong and repeated pressure and repeated washing with the solvents usually employed for removing impurities. No anthracene yielding less than 20 per cent. of crystals by the above test should, says the author, be found in the market. M. M. P. M.

Anthracene-testing. By C. CASPERS (*Chem. News*, xxxiv, 211).—The alcohol and carbon disulphide processes were intended to indicate merely the insoluble portion of the mixed hydrocarbons sold as anthracene, and are now disused.

The author objects to multiplying the amount of anthraquinone found by the oxidising process by 0.856; the anthraquinone is really the valuable product obtainable from anthracene, and the hydrocarbon would soon find its market value if estimated according to the anthraquinone obtainable from it. He also criticises Versmann's method of estimating anthracene as anthraquinone, and asserts that, the melting points of his anthraquinones not being constant, no dependence can be placed on the method. The whole of the anthraquinone does not crystallise out from the glacial acetic acid, and the powder precipitated on addition of water does not consist of pure anthraquinone.

W. B.

Action of Iodine on Carminic Acid and on Hæmatin. By A. FRÉBAULT (*J. Pharm. Chim.* [4], xxiii, 338—340).—Iodine, or potassium iodide, in presence of alkalis, destroys the red colour of tincture of cochineal and that of hæmatin, the colouring matter of logwood. The author proposes to replace Penny's process and others by employing this reaction in testing carmine, in determining hæmatin in logwood, and in estimating iodine. The use of very dilute solutions is recommended as exhibiting the reaction with the greatest distinctness. R. R.

Testing of Oils. By A. PINCHON (*J. Pharm. Chim.* [4], xxiv, 29—33).—The author proposes to use for each kind of oil (or other liquid) a special areometer, the graduation on the stem of which shall mark the immersions of the instrument at each degree of ordinary temperature, when placed in a pure sample of the particular oil. A small thermometer is made to form part of the instrument itself, so that the temperature of the liquid in which it is immersed is at once indicated.

R. R.

The Reagents for Alkaloid Separations. By R. GODEFFROY (*Arch. Pharm.* [3], ix, 147).—Antimony trichloride forms white or yellow precipitates in hydrochloric acid solution of aconitine, atropine, quinine, cinchonine, piperine, strychnine, and veratrine, but not of caffeine or morphine.

Similar solutions of aconitine, piperine, strychnine, and veratrine are precipitated (yellow or red) by ferric chloride; atropine, quinine, cinchonine, caffeine, and morphine are not precipitated.

M. M. P. M.

Estimation of Barley in Oatmeal. By PATTINSON and STEAD (*Chem. News*, xxxiv, 194).—The first method depends upon thoroughly mixing the sample, sifting it, making a quantity into a paste with water, examining under the microscope, and counting the number of barley granules in a given field. By comparison with standard meals, the amount of barley may be very accurately determined. For carrying out the process, the details of the original paper must be consulted.

The second process, which the authors employ along with the first, consists in sifting the meal and picking out the hard particles of barley from the coarser portion, by the aid of a lens and the finger-nail. Both methods give good results.

M. M. P. M.

Butter Analysis. By C. ESTCOURT (*Chem. News*, xxxiv, 254—255; xxxv, 10).—In ascertaining the presence of, and estimating the quantity of foreign fat in butter, either by the fatty acid or by the ordinary specific gravity method, several difficulties present themselves, the former being objectionable on account of the possible loss in manipulation and the time occupied, and the latter on account of the extreme care necessary in taking gravities at so high a temperature as 100° F., by means of the bottle. (A degree more or less is quite equal to 0.5 in the gravity.) The author was, therefore, led to try whether the density of fats could be taken by means of a specific gravity balance working by immersion, the tube containing the fats being kept at a constant temperature. The water- or steam-bath was found to answer, with the only inconvenience that the steam constantly deposited on the beam of the balance. It was, therefore, necessary to devise a method free from this inconvenience. The bath used in these determinations is simply a cylinder (5 inches by 4 inches), closed at both ends. In the top, or cover end, two holes are cut, one small, for filling the bath and permitting escape of steam, &c.; the other, an oval (3 inches by 2 inches), into which is fixed a smaller

oval tube closed at the bottom only, and resting inside the large cylinder.

The large cylinder is filled with water, the small tube with paraffin, in which are immersed the tubes of fat and a thermometer. Heat is applied to the outer cylinder, and when the thermometer indicates the constant temperature, the specific gravity is taken by immersion. Specific gravity beads may also be used, at least, as indicators of the purity or impurity of the butter under examination. All that is necessary is a large beaker kept full of water boiling, and supporting in it the tubes full of the fat to be examined.

Three beads, one of which would float just under the surface of pure butter-fat, one just under the surface of a 50 per cent. mixture, and one under the surface of beef-fat (all tested at boiling heat of water), would at once give an approximate idea of the amount of adulteration of the sample in which they were tried. The author then advises, as the best practical method of estimating fairly the percentage of adulteration, that, after the gravity has been obtained, a determination be made of the fatty acid.

D. B.

Hyposulphite of Sodium (SO_2Na_2) as a Reagent in the Analysis of the Colouring Matters of Dyed Stuffs. By G. SCUTARI-MANZONI (*Gazzetta chimica italiana*, vi, 318).—From many experiments detailed in a former memoir, it appeared probable that this substance would be a valuable reagent in the examination of the nature of a colouring matter. Among natural dyes the blue from indigo, the violet and red from litmus, and the red from Brazil wood, are the only ones which are as sensitive to this test as the blue, violet, and red derived from other substances. A cloth dyed with litmus is bleached instantaneously, even in the cold, by a solution of hyposulphite. A cloth dyed with Brazil wood is bleached after a very short time. Another, which had been dyed with indigo over another colour, was digested with hyposulphite, and after some time exhibited the under colour only. The reaction is facilitated by rendering the liquor alkaline with potash or soda and by heating, but not to boiling. The rapid oxidation of this bleaching reagent renders it of little value in the determination of the amount of litmus in the commercial substance and in tinctures.

F. D. B.

Estimation of Wool in Yarn. By K. J. BAYER (*Zeitschr. Anal. Chem.*, 1876, 205—207).—About 0.5 to 0.8 grm. of the material, having been dried at 100° to give the moisture, is digested in the cold for 12 hours, with 200 c.c. of sulphuric acid (4 vols. of acid to 1 of water). The liquid is then poured off, and the substance further treated with a like quantity of acid for four or five hours. This will completely dissolve all the cotton present. The two liquids are now diluted, each with six times its bulk of a mixture of equal volumes of water and alcohol, and then filtered. If the original material were coloured, the products of the colouring matter must be washed out with hot absolute alcohol. The substance is subsequently washed with boiling water until free from acid, dried at 100° , and weighed.

The weight, less 2 per cent., gives the amount of wool. The colouring matter in coloured fabrics amounts to about $3\frac{1}{2}$ per cent.

F. J. L.

Technical Chemistry.

Deacon's Process for the Preparation of Chlorine. By K. JURISCH (*Dingl. polyt. J.*, cxxi, p. 356—384).—This process has not been found to answer the purposes of the bleaching powder manufacturer, so well as to place it in the position of pre-eminence which at first it was expected to fill. The reason of this is, that the clay-balls soaked in copper solution, after a comparatively short period of activity, lose their power of decomposing the hot hydrochloric acid gas. This period of activity, moreover, becomes shorter the oftener the balls are freshly soaked with copper solution. This drawback, added to the costliness of the plant required, gives the advantage to Weldon's process.

The author attempts to solve the problem as to what the causes are, whereby after a certain time, the clay-balls saturated with copper-salt lose their capacity for decomposing hydrochloric acid gas. Manufacturers using this process found that nearly the same quantity of bleaching powder was obtained, whether they worked quickly or slowly. This quantity amounted to about 600 tons of powder per 120 tons of saturated clay-balls, with about 1 per cent. of copper. This amount being obtained, the decomposition of the hydrochloric acid sank to about from 10 to 20 per cent., so that the process had to be stopped, in order to fill up with freshly soaked balls. The copper solution for soaking the balls contained 3 parts by weight of cupric sulphate to 1 part sodium sulphate. The temperature employed in the process in Newcastle was 450° to 500° ; in Widnes, 390° to 415° . It was found that, at the end of a period of activity, the loss of copper by volatilisation only amounted to from 15 to 25 per cent., and therefore the inactivity of the balls must be traced to some other causes than this mere loss of copper. The most probable chief cause is considered to be the gradual envelopment of the copper salt on the balls, by foreign inactive substances, carried along with the gases. These impurities arise chiefly from the impure sulphuric acid used in the decomposing process. Amongst these the sulphates of iron and alumina, chloride of iron, and arsenic compounds are the most abundant.

Hurter has found, in the decomposition by heat of common salt with the common sulphuric acid containing arsenic, that, in the first eighth part of the hydrochloric acid passing over, there are contained 50 per cent. of the total arsenic of the sulphuric acid, and in the first half almost the whole of this arsenic. The mass of acid sulphate in the salt cake-pot, before showing through into the furnace, was found to be completely free from arsenic.

Another evil influence was found in the sulphuric acid evaporated,

and carried over from the pot or furnace. It was found that, when sulphuric acid was most abundantly present, the decomposing action was speedily reduced. It would therefore be better that the salt should be decomposed at lower temperatures, say 20° to 100° . The objection to this would be that the cast-iron of the pots would suffer, the salt could not be completely decomposed, and the work would be slower. On testing the gas at different stages of the process, it was found that, in the early stages but little sulphuric acid passed over, but towards the end of the boiling of the charge, the amount passing over began to be large. It is recommended therefore to use only that gas which comes off in the early stage, and is consequently freest from sulphuric acid. The furnace gas is also not so safe to use, because it contains, besides a maximum of sulphuric acid, also most of the other volatile compounds which were contained in the sulphuric acid.

Hurter has found that the quantity of chloride of lime which can be manufactured in a given time, under ordinary conditions, is proportional to the amount of bases (ferric and aluminium oxides) contained in the clay of the balls. A highly silicated clay gave the worst production. It is therefore, says the author, a question of life or death for the process, whether the sulphuric acid can be removed from the gas, or, failing this, a large quantity of basic matter introduced, to act as carrier for the active decomposing substance. Some experiments are next described with an apparatus in which an attempt is made to realise the Deacon's process on the small scale. In a more recent paper this apparatus is, however, acknowledged to have yielded results from which comparisons cannot be drawn.

Hasenclever and Sartori found that sulphuric acid vapours, in contact with hot aluminium sulphate, decompose, giving sulphur dioxide, steam, and oxygen. Aluminium sulphate is found largely as a chief constituent of the enveloping matter collected about the clay balls. The sum and substance of all the experiments tried was to show that sulphuric acid in the gaseous form exerts a chemical action during the process, very damaging to the latter, and also that an envelopment of the clay balls with which the apparatus is charged, by non-active substances, gradually takes place. These two influences together contribute chiefly to the failure of the process of decomposition.

W. S.

Note by Abstractor.—More recently Jurisch has written (*Dingl. polyt. J.*, cxxii, 366—370), acknowledging the probable inadequacy of the apparatus with which his experiments were tried, as a reproduction of Deacon's process on the large scale. He adds further, that he took as a measure for the activity of the apparatus, the magnitude of the percentage decomposition of the hydrochloric acid into chlorine and water, forgetting that the absolute quantity of chlorine produced in the given time may also just as well be regarded as a measure of this activity. With respect to the conclusions arrived at as to the extent of the damage done by the volatilised sulphuric acid, and the enveloping substances referred to, Hurter has stated that these conclusions are very questionable.

The magnitude of the decomposition of the hydrochloric acid into chlorine and water, expressed in per cents. of the weight of hydro-

chloric acid employed, is mainly dependent on three variable circumstances:—

1. The proportions in the mixture of hydrochloric acid gas and air.

2. The velocity of the current of gas.

3. The temperature of the clay balls and of the gas.

1. The proportions in the gaseous mixture of hydrochloric acid and air vary between 20 and 60 per cent. by volume of hydrochloric acid in the mixture. Hurter has shown that the decomposition falls with a smaller proportion of air, and rises with an increased proportion.

2. On increasing the velocity of the current of gas, other things being equal, the decomposition falls, and recovers with a decreased velocity.

3. By raising the temperature, the decomposition is increased, and *vice versâ*, other circumstances remaining constant.

It was in taking into account the above conditions, and realising the whole in a small laboratory reproduction, that the element of doubt arose as to the applicability of the results arrived at.

Hurter states that he has already tested the effect of the presence of sulphuric acid (as prepared by Jurisch, in his small apparatus) in the gaseous current, and found it not injurious. He is also of opinion that sulphuric acid is injurious only in the same degree as arsenic and antimony are, in acting upon the copper, and forming inert substances. But Jurisch's experiments are insufficient to show that the sulphuric acid possesses an injurious influence whilst in the state of gas.

W. S.

Extraction of Silver by means of Calcium Thiosulphate. (*Dingl. polyt. J.*, cxxii, 177—180).—The ores are in the first place subjected to a chlorinating process, after which they are brought into round wooden tubs which are 1·2 m. high and 2·7 m. in diameter. Each tub holds about 2 tons of ore, and is furnished with an agitator and a closely-fitting cover with two ventilators for the conveyance of steam and sulphurous acid. The tubs are filled with the ore and the latter treated with Hunt and Douglas's liquid (consisting of sodium chloride and ferrous chloride). The mixture is then agitated, and at the same time sulphurous acid and steam introduced. The whole of the cupric oxide present in the ore is thus dissolved by the ferrous chloride. The reason for the addition of sulphurous acid is that the ferrous chloride would otherwise be converted into ferric chloride by the oxidising ingredients present in the ore, and the copper would then be precipitated. The cupric chloride in presence of sodium chloride converts the whole of the argentic sulphide present in the ore into the chloride. After having agitated the mixture in these tubs for five hours, the solution is allowed to settle and then drawn off. The tubs are again filled with water, steamed and agitated. After two hours' washing with hot water, the apparatus is again stopped and the clear water drawn off. Calcium thiosulphate is now added from a reservoir placed above the tubs, and after agitation for four hours at 38°,

the mixture is allowed to settle and the clear silver solution drawn off. In the case of ores being very rich in precious metals it is advisable to repeat this operation before washing with warm water at 40°. Finally the tubs are emptied.

The solution containing the sodium chloride and ferrous chloride is passed through a filter in order to separate mechanical impurities, and is then run into tanks filled with iron filings, where the copper in solution is precipitated and the solution brought back to its former condition. The washings are evaporated to 15° B., and have to undergo a similar treatment. The silver solution is placed in large precipitating vessels, treated with calcium sulphide, agitated for a few minutes, and left to deposit. The liquid is then run into the regenerating vessels and treated with sulphurous acid, which converts the whole of the excess of calcium sulphide used into the thiosulphate. The washings from the treatment with calcium thiosulphate are worked up in a similar manner. When the precipitate in the precipitating vessels is from 125—150 mm. high, it is washed with hot water, dried, and roasted in a small reverberatory furnace at a low temperature, until all the sulphur has been driven off. Fluxes are added if necessary, and the temperature is raised until the whole mass is in a state of perfect fusion. The slags are then removed, and the pure metal skimmed off and put into forms. If the slags contain more than 20 ounces of silver per ton they are worked up again with the ore.

The following is a list of the costs for working one ton of ore, exclusive of the costs for grinding and chlorinating:—Labour, 1·87 dollars; fuel, 1·13 dollars; chemicals, 1·60 dollars; roasting, and fusing, 1·20 dollars; total, 5·80 dollars. D. B.

Presence of Sulphocyanates in Commercial Soda. By R. NITZKI (*Arch. Pharm.* [3], ix, 41—46).—Crude soda contains, on an average, about $\frac{1}{2}$ a per cent. of sodium sulphocyanate and 0·8 per cent. of sodium ferrocyanide. The finer salt is probably formed by the action of sodium sulphide upon sodium cyanide, both of which are always present in crude ley. The sulphocyanate is present in considerably larger quantities in the last quantities of soda which separate from the mother-liquor. The author estimates the quantities of sodium ferrocyanide and sodium sulphocyanate annually turned out in the soda-salts of a work making 15,000 kilos. soda daily, as equal to 6,500 and 3,250 kilos. respectively. M. M. P. M.

Alum-meal. (*Dingl. polyt. J.*, cxxi, 390).—A new method for the preparation of alum has been described by J. Zimmermann. The raw material used contained:—Alumina, 17 to 18 per cent.; potash, 2 to 5 per cent.; silica, 50 per cent.; water, about 30 per cent. When dried in the air, this substance contains about 7 per cent. of water. On treatment with sulphuric acid it loses 22·65 per cent. of alumina and 11·23 per cent. of potash, dissolved by the sulphuric acid.

The material is mixed with sulphuric acid of 1·525 specific gravity, and allowed to stand for three to four weeks, then lixiviated, the

solution concentrated, and the alum-powder precipitated by addition of potassium or ammonium sulphate. W. S.

So-called Plastic Dinas-crystal. By C. BISCHOFF (*Dingl. polyt. J.*, cccxi, 345).—The sample operated upon by the author was obtained from the Bonner Portland Cement Works of Drs. Rieth and O'Brien. It is a faint greyish, heavy powder, the bulk of which consists of fine colourless gritty particles, with coarse angular fragments of quartz both white and yellow. The coarser particles constitute about 25 per cent. of the whole. On digestion with water, a small quantity of lime is extracted, giving a faint alkaline reaction to the solution. On treatment with hydrochloric acid, a few bubbles of gas escape, apparently proceeding from the coarser particles. If a quantity of the substance is tempered with water, a paste is obtained which moulds well in a few hours, and gradually becomes as hard as clay. If the paste be made as stiff as dough, then left to dry in the air, and finally dried at a temperature gradually rising to 170°, the linear shrinking of the mass amounts to from 4.5 to 5 per cent.

When the completely dried and tolerably solid mass was heated to bright redness, it became as hard as stone and sinterised, but still somewhat inclined to absorb moisture. It had a spotless uniform yellowish-grey colour, and a granular structure. In the mass the coarser particles of quartz were still perceptible. The mass was free from cracks, and remained quite unaltered in volume. It had neither shrunk nor swollen.

When the heat was still further increased, so as to be sufficient to melt platinum, the sample was found to be strongly glazed outside, but inside was full of cavities. When the material was very finely pulverised, and then strongly heated, it fused to a frothy glass, the outside glazed and shining, but inside it is quite full of round holes. The substance dried at 100° contained :

Al_2O_3	Fe_2O_3	CaO.	Loss on heating (water).
4.66	2.62	1.08	3.96 = 99.80

The valuable property of this substance is, that when completely dried, it may be burnt without alteration of volume, does not crack, and neither shrinks nor swells out. It has also great plasticity and capacity for moulding. W. S.

Manganese Bronze. (*Dingl. polyt. J.*, cccxi, 334).—This is an alloy of ordinary bronze and manganese, which has been very successfully applied in the Woolwich cannon foundry. The details of its manufacture are not yet known. The manganese has the effect of ridding the bronze of all oxides, and conferring upon it a homogeneous, densely-granular structure, and thus increased strength, together with greater tenacity and hardness. A tolerably large ingot of this manganese-bronze exhibited on fracture a fine-grained structure like that of steel. The hardness of the bronze can be still further increased. The colour is like that of good cannon-metal, but more

lustrous, and gold-like. At a red-heat the bronze can be forged, rolled into bars and plates, and drawn into wire and tubes. Experiments proved that a bar of one variety of this bronze possessed nearly equal capacities of absolute firmness and extensibility to those of bar iron of medium quality, whilst its limit of elasticity was higher. All forged samples surpassed the best bar-iron in firmness and extensibility, and in these respects they stood on an equal footing with steel of soft quality.

W. S.

Ash of hard Carbon from Coal-gas Retorts. By W. VAN SLOOTEN (*Chem. News*, xxxiv, 190).—This carbon is well suited for laboratory furnaces in which a very high temperature is required. The ash varied from 0.35 to 3.77 per cent.: the ash of the last mentioned specimen consisted of—

SiO ₂ .	Fe ₂ O ₃ .	Na ₂ O.	Li ₂ O.	Cl.
42.0	47.0	8.57	trace	3.72 = 101.29

M. M. P. M.

Composition of an Iron Deposit. By G. PATERSON (*Chem. News*, xxxiv, 198).—The deposit was from an open drain on Locharmoss, bordering on the Solway Firth. Large quantities of this deposit are seen upon the surface of this district. The deposit was dried at 100°, and then gave the following numbers:—

Organic matter + H ₂ O.	Fe ₂ O ₃ .	FeO.	CuO.	MgO.	SO ₃ .	P ₂ O ₅ .
50.74	43.29	3.58	0.51	0.10	1.29	0.18

S.	Soluble SiO ₂ .	Sand.
0.15	0.31	0.65 = 100.80.

M. M. P. M.

Effect of Sulphate of Alumina on Sewage. By A. McD. GRAHAM (*Chem. News*, xxxiv, 197).—The author holds that the addition of sulphate of alumina to sewage causes the precipitation of phosphoric acid, albuminoid substances, and the fatty acids of soap, together with suspended matter.

M. M. P. M.

Experiments on the Alcohol from Barbary Figs. By BALLARD (*J. Pharm. Chim.* [4], xxiii, 100—105).—The juice expressed from 33 kilograms of Barbary figs weighed 11 kilograms. It had an insipid sweet taste, and a sharp unpleasant smell; its colour was brownish-red. Its specific gravity was 6° B.; it contained acid equivalent to 2.8 grams of sulphuric acid (H₂SO₄) in 1000 c.c., and 128 grams of sugar per litre. It was left to ferment at 25° for 8 days. The fermentation stopped in a bottle exposed to a temperature of 45—54°, but re-commenced at a lower temperature. The results are given in the following table:—

	Temperature of liquid.	Density.	Acid p.c.	Sugar p. litre.	Alcohol p.c. at 15°.	
1st day....	26°	1.044	2.8	125	—	—
2nd „	26	1.042	2.8	125	—	Liquid clear.
3rd „	25	1.041	—	—	0	Fermentation begun.
4th „	25	1.039	—	—	—	In progress.
5th „	25	1.023	7.8	55	—	Active.
6th „	25	1.006	7.8	4	4.1	Slower.
7th „	25	1.004	—	0	4.2	None.
8th „	25	1.003	9.8	—	4.2	—

Two days after fermentation had stopped, the liquid was distilled from a water-bath. The alcohol, after one rectification, showed 85°, was colourless and very mobile, had a smell of kirsch, and a pleasant fruity taste, with a slight empyreumatic taste, which diminished on keeping.

In a second experiment, 10 kilograms of juice were obtained from 21 kilograms of figs. Its specific gravity was 1.007 to 1.047; its acidity 5.6 to 8.4 grams, and its contents of sugar 6 to 14 grams per litre. After two months, its colour had nearly disappeared, and its surface was covered with a pellicle of mycoderma; its specific gravity was 1.007; alcoholic strength, 4.2; acidity, 13 per cent.

6.8 kilograms of figs, in a third experiment, gave 4.1 kilograms of juice; during fermentation, the following changes were observed:—

	Specific gravity.	Acid per litre.	Sugar per litre.	Alcohol p.c. at 15°.	
1st day....	1.047	1.4	140 grams	—	—
2nd „	—	1.9	—	—	Liquid became clear.
3rd „	—	3.1	—	—	Fermentation visible.
4th „	—	4.2	—	—	Fermentation in progress.
5th „	—	5.6	—	—	Active.
6th „	—	7.0	—	—	—
7th „	—	7.5	—	—	Slow.
8th „	1.007	8.5	0	4.5	None.

From these experiments it is seen that Barbary figs contain a considerable proportion of grape-sugar; that they yield about two-thirds of their weight of juice, which is thoroughly fermented in a week, and contains about 4.5 per cent. of absolute alcohol, or 3.57 grams per cent. But theory demands 5.8 to 6.5 grams per cent., or in volume 6.9 to 8.0. Whence arises this loss of alcohol? The juice, evaporated on the water-bath, gave 45 p.c. of extract, which, when treated with boiling alcohol, yielded 34 grams of mannite. The juice had thus undergone mannitic as well as alcoholic fermentation, the former being the more energetic of the two.

With the view of hindering this mannitic fermentation, three experiments were made. In the first case, 1 gram of tannin per litre was

added; in the second, 5 c.c. of hydrochloric acid; and in the third, 3 c.c. of sulphuric acid. The temperature was kept at 30°. The fermentation began on the second day. In 5 days, the first two liquids contained 4.5 and 6.2 per cent. of alcohol; in 18 days, the last sample contained 4.5 per cent. of alcohol. Thus it is seen that mannitic fermentation can be converted into alcoholic by addition of tannin or hydrochloric acid. From 100 litres of juice, representing 160 kilograms of figs, 7 to 7½ litres of 85 per cent. alcohol can be made.

It thus appears that these figs, which grow on the rockiest soils of Algeria without cultivation, may be used profitably as a substitute for roots or cereals in manufacturing alcohol; the extraction of the juice is easy, its fermentation is spontaneous, and the residues may be used as food for cattle.

W. R.

The use of Phosphoric Acid in the Manufacture of Beet-sugar. By O. VIBRANS (*Dingl. polyt. J.*, cxxi, 389).—The employment of phosphoric acid is strongly to be recommended, especially in cases where a considerable amount of non-saccharine matter exists in the beet-juices. At the commencement of the process of working up the beet-juice, the phosphoric acid has little influence: it may, indeed, act injuriously, in causing the juice to foam too strongly, and evaporate turbulently.

Comparative experiments at the end of September and February yielded the following results:—At the end of September, 2 litres of phosphoric acid of 20 per cent. were added to the separation-pan containing 1,300 litres of juice of 10.23 per cent. of sugar, according to Brix's* table. The composition of mud obtained, compared with a mud obtained in a second experiment without using phosphoric acid, was as follows:—

	With phosphoric acid.		Without phosphoric acid.
Water	50.97	50.25
Carbonic acid	13.28	13.06
Sugar	1.30	1.27
Ash.....	15.86	16.34
Organic matter	18.59	}	19.08
Nitrogen in the above	0.44		0.46

The beets themselves gave the following results:—

	Per cent.	
Brix	= 18.13	Quotient, 86.87.
Sugar....	= 15.75	On 10 parts of sugar, 15.11 parts non-sugar.
Non-sugar = 2.38		

At the end of February, the following experiments were repeated—(I) with, and (II) without, phosphoric acid; 4 litres of phosphoric acid were, however, employed to 1,300 litres of juice.

* *Note by Abstractor.*—Brix's table is one constructed upon the basis of the relationship of the specific gravity to the centesimal content of sugar in saccharine solutions.

Beet Juice to be Separated.

	I. Per cent.	II. Per cent.
Brix	9.71	9.22
Sugar	8.75	8.01
Non-sugar	0.96	1.21
Nitrogen in the above ..	0.073	0.058

Separated Juice.

	I. Per cent.	II. Per cent.
Brix	8.89	8.05
Sugar	8.23	7.11
Non-sugar	0.66	0.94
Nitrogen in the above ..	0.029	0.028

Mud.

	I.	II.
Water	47.77	50.33
Sugar	1.66	1.86
Carbonic acid	11.36	16.96
Ash	13.49	12.29
Organic matter	25.72	18.56
Nitrogen in the above	0.37	0.33

The beets employed in the above experiments contained:—

	Per cent.	
Brix	15.78	Quotient, 80.16.
Sugar	12.65	On 10 of sugar = 24.74 non-sugar.
Non-sugar ..	3.13	

These comparative experiments show that the phosphoric acid is employed with advantage, where the working of the juice is rendered difficult by the presence of much non-saccharine matter. Vibrans considers that so much phosphoric acid should be added, that the alkalinity shall not fall below 0.03 to 0.025 in the separated beet-juice. If the proportion is increased further, little or no more precipitation of organic matter takes place in the separation-time, phosphate of lime is unnecessarily formed, the juices acquire a tendency to foam on boiling down, and this tendency increases still more in the vacuum-pan.

W. S.

Experiments to demonstrate the Conversion of Sugar when added to Fermenting Must and Marc of Grapes. By Bous-singault (*Ann. Chim. Phys.* [5], vii, 433—451).—Attempts to prepare artificial wines have hitherto been unsuccessful, owing probably to the want of exact knowledge of the essential constituents of natural

wines. But an attempt was made so long ago as 1776 to raise the percentage of alcohol in wines by addition of sugar before fermentation. This produced a depreciation in the demand for Burgundy wines, for the sugar added was prepared by boiling starch with dilute sulphuric acid, and the bye-products gave a disagreeable flavour to the wines. A compact was therefore made among the vine-growers to discontinue this practice. Some of them, however, did not agree with this change, but maintained that sugar prepared from the cane, or from beetroot, was not prejudicial to good wines. One of the reasons for adding sugar was to counteract the acidity of wines, arising from the presence of acid potassium tartrate, and also from succinic, acetic, malic, and other free acids. These acids cannot be neutralised by alkalis, or by alkaline earths, for their salts have a disagreeable taste. Neither is the acidity really counteracted by addition of sugar. There is only one means of lessening this acidity, viz., by addition of water. This is, of course, useless in the case of good vintages, but when a bad vintage takes place, a drinkable wine may often be made from a very bad wine. This was done by the author in 1856. The acidity of the wine was equivalent to 9 grams of sulphuric acid per liter—double of what is the case in favourable circumstances. The author diluted each hectoliter of must with a hectoliter of water containing 20 kilograms of white sugar in solution. After a year the wine was ready for use. Its acidity was equal to 4.75 grams of sulphuric acid per liter, and the percentage of alcohol was 8.

The price of a hectoliter of this wine was 22 francs, while that of the most ordinary was 50 francs.

It would be advantageous to use sugar from grapes themselves, instead of cane sugar, for it would contain the essential flavouring matter of the wine. The vine contains more sugar than any other plant except the *Agave americana*.

From experiments on the amount of sugar converted into alcohol by fermentation, the author discovered that, on addition of sugar, 82 per cent. of the sugar was converted into alcohol; the remainder was converted into succinic acid and glycerin, and probably some of the alcohol was destroyed by the action of ferments, such as *Mycoderma aceti* and *Mycoderma vini*.

Joseph Boussingault has experimented on the actual yield of alcohol from the sugar contained in various fruits, and constructed the following table, the theoretical yield being expressed by 100.

	Alcohol.
White grapes from Lampertsloch	91.
Red.....	91
Cider apples	89
"	90
"	89
Wild cherry	92
Black cherry	88
Small yellow plums (mirabelles)	48
" " "	71

	Alcohol.
Damsons.....	91
Juice from ditto	94
" " 	78
Sorbs	90
Honey.....	91

From these experiments it appears that to obtain 1 liter of absolute alcohol, 1.477 kilos. of sugar are necessary; in practice, 1.802 kilos.

A comparison is also given of the acidity, amount of alcohol, water, and fixed residue in wine, and in the juice of the marc to which sugar has been added.

W. R.

Preparation of Anthraquinone by the Action of Chloride of Lime Solution and a Metallic Salt on Anthracene. By A. HENNIGES (*Dingl. polyt. J.*, cccxi, 351). The anthracene used contained 40 per cent. of sublimed anthracene. A portion of this was mixed with 10 per cent. of manganese chloride, and the mixture was stirred up with water to a thick paste and heated nearly to boiling. Into this a solution of chloride of lime was slowly run. The precipitated oxide of manganese, being finely divided and uniformly mixed with the anthracene, acted as a carrier of oxygen from the chloride of lime to the anthracene; after three hours all the anthracene was oxidised. The metallic oxide was extracted with sulphuric acid, and the crude quinone purified by sublimation. It was found that this quinone contained chlorine. An effort to form dichloranthraquinone by employing still more chlorine in a repetition of the experiment was unsuccessful. On fusing the product with potash, no alizarin was obtained, but on treating it with sulphuric acid, a brown humus-like body separated out in small quantity, and the anthraquinone remained contaminated with chlorine. Instead of manganese chloride, platinum and cobalt chlorides were next employed. The anthraquinone obtained was in each case contaminated with chlorine. In the case of the manganese chloride, the action is most expeditious, but most of the chlorine-product is thus obtained at the same time. Cobalt chloride acts very slowly, and a small quantity of the anthracene is not oxidised to anthraquinone, and must be separated therefrom by alcohol. After cobalt chloride ferric chloride acts most energetically, then cupric chloride, less strongly platinum chloride. It appears that the chlorine is not contained in the anthraquinone, but is a chlorinated bye-product.

For the preparation of anthraquinone by the action of nitrates on sublimed anthracene, equal parts of anthracene and nitrate of iron were moistened with water and exposed to a temperature of 100°. After 12 hours the conversion into anthraquinone was complete. This anthraquinone was found to be contaminated with nitro-products. 10 grams of anthracene gave 3 grams of sublimed anthraquinone. The preparation of anthraquinone was next attempted by the action of manganese dioxide and dilute sulphuric acid on sublimed anthracene. The manganese was finely pulverized and passed through a hair sieve. Equal parts by weight of the manganese powder and anthracene were intimately mixed, moistened with water, and then

treated with a mixture of equal volumes of sulphuric acid and water. A lively reaction commenced, and later on this was assisted by warming on the water-bath. After 12 hours all the anthracene was converted into anthraquinone. Sulphuric acid was added till all the manganese was dissolved. From 100 grams of anthracene 110 grams of anthraquinone were obtained. The crude quinone obtained as above could only be purified by sublimation.

The research was made in the hope of hitting upon a cheaper method of oxidising anthracene than by means of chromic acid. The oxidation with chloride of lime and a metallic salt is not recommended as a manufacturing process, as the chlorine product formed makes it difficult to purify the anthraquinone, and this product yields no alizarin. Metallic chlorides give too little anthraquinone. From nitrate of iron too little is obtained, and this is impure, from the presence of nitro-compounds. The only objection against the method with sulphuric acid and manganese dioxide is that the crude quinone obtained cannot be purified by the wet method. A purification by means of sublimation appears to present technical difficulties: it is just a question if these can be removed.

W. S.

Black-blue Colour for Paper. By A. ABADIE (*Dingl. polyt. J.*, cccxi, 391). The author has obtained nine kinds of black-blue dye for common kinds of paper, arranged according to their respective depths of tint, from the brightest, a greenish-blue, to a very beautiful glowing black-blue. It is not to be forgotten that this colour is used for badly-boiled and unbleached stuff, and all the commonest varieties. The quantities given underneath are sufficient for 100 kilos. of dry paper. Alum or aluminium sulphate must not be employed for the precipitation of the resin or fat soaps; cupric sulphate answers instead, and the quantity of size employed must therefore stand in right proportion to the amount of cupric sulphate used.

No. Kilos.

1. { 1.50 Cupric sulphate.
3.00 Campeachy extract.
2. { 1.25 Cupric sulphate.
2.50 Campeachy extract.
0.50 Bone-black.
3. { 0.75 Cupric sulphate.
1.50 Campeachy extract.
1.50 Common-salt.
0.25 Bone-black.
4. { 1.00 Cupric sulphate.
2.00 Campeachy extract.
1.50 Bone-black.
5. { 1.00 Cupric sulphate.
2.00 Campeachy extract.
6.00 Pyroligneous acid.

No. Kilos.

6. { 1.50 Cupric sulphate.
3.00 Campeachy extract.
2.00 Bone-black.
7. { 1.50 Cupric sulphate.
3.00 Campeachy extract.
2.00 Bone-black.
8. { 3.00 Pyroligneous acid.
3.00 Cupric sulphate.
4.00 Campeachy extract.
9. { 4.00 Cupric sulphate.
6.00 Campeachy extract.

W. S.

Rapid Destruction of Linen Cloths. (*Dingl. polyt. J.*, cccxi, 386). A number of napkins and table-cloths were handed over to

Professor Birnbaum of Karlsruhe, by an hotel proprietor for examination. After only one and a half year's use they had become extremely tender and worn. On examination with the microscope it was found that the threads were strongly encrusted, and the incrustation was further found to consist almost entirely of calcium carbonate. The effect of this mineral matter between the fibres of the cloth would be to wear them away by the excessive friction thus induced. The question next following was, who had introduced the substance into the material, the seller or the buyer? The manufacturer having handed over a quantity of the cloth, the amount of ash in a weighed portion of this was determined, and found to vary from 0.32 to 5.34 per cent., whilst the ash in the above-mentioned damaged cloth amounted to 0.38 per cent. Hence the increase of mineral matter must be due to some treatment on the part of the buyer.

It accidentally occurred to Birnbaum that in many hotels a practice is prevalent of freshening up the napkins by simply moistening with lime-water and pressing. The coating of lime thus thinly spread over the fibre of the cloth gives it a somewhat hard feeling and a certain finished appearance, which makes the articles appear as if they had been freshly washed. By repeated use of this method the cloth certainly becomes very much tendered.

A piece of linen cloth which had been thus moistened with lime-water some thirty times and then dried again, washed with soap from time to time, and then again moistened with lime-water, exhibited exactly the "tender" properties which characterised the cloths in question. A warning is accordingly given against the adoption of such a finishing process.

The crystals of calcium hydrate formed in the fibre of the cloth rupture the cells, and thus weaken the texture; the absorption of carbonic acid leads to an increase of bulk, and thus further damage ensues; and finally, the calcium carbonate formed acts injuriously, as it increases the friction. Thus by mechanical means alone much damage is done, quite apart from the effect induced by the caustic action of the calcium hydrate. W.*S.

Causes and Prevention of Stains, Spots, and other defects in Dyed Cloths. (*Dingl. polyt. J.*, cxxii, 180—182).—These defects in dyed materials are mostly due to a bad treatment of the cloth, which is not sufficiently washed when taken out of the soap bath. The existence of stains or spots before dyeing may easily be proved by passing it through hot water several times and observing whether the water is absorbed by every part of the cloth. If such is not the case, it is best for the dyer to return the cloth, so that it may be filled again. Dark spots, which are often found in dyed cloth, are mostly to be attributed to some irregularities in the shrinking operations with steam, and are due to the steam carrying condensed water into the rolling cylinders. It is therefore necessary to work the steam at a pressure higher than that of three atmospheres, in order to have less condensation, and to use water which is not largely contaminated with mineral constituents. The drying operations are very often the cause

of these defects, and it is best to dry the material in a centrifugal machine, and not to leave it exposed to the water for a very long time. D. B.

The Solution of Caoutchouc. (*Dingl. polyt. J.*, cxxi, 391). Heeren has determined the solubility of 12 important kinds of india-rubber in benzene. The samples were first worked between hot rollers, then cut into thin strips; these were treated in small flasks with some benzene and allowed to stand for some time. The addition of benzene was then gradually continued, with frequent shaking, till all the samples had attained a very tenacious consistency. This same degree of consistency it was sought to attain in the case of all the samples. This being done, small quantities of the solutions were weighed out in tared watch-glasses, and then allowed to evaporate in a heated drying chest; the residues were finally weighed. The following numbers were thus obtained:—

	Percentage content of solution.	Or, 100 of benzol had taken up
Guaiaquil	20.0	25.0 caoutchouc.
Para	17.0	20.0 "
Carthageria	16.1	18.0 "
Borneo	13.8	15.0 "
Africa	12.7	14.5 "
Ceara	12.0	13.6 "
Mozambique	11.5	13.0 "
Rangoon	9.1	10.0 "
Quisembo	9.0	9.8 "
Africa-knökels	8.6	9.4 "
Africa-niggers	7.8	8.5 "
Madagascar	5.7	6.0 "

Of course since the coinciding of the degrees of density of the thick fluids obtained is merely a matter of measurement by the eye, the results can be looked upon only as approximating to the truth.

W. S.

The Present State of the Rice-starch Manufacture. By M. ADLUNG (*Dingl. polyt. J.*, cxxi, 543—548).—Although the methods already described (p. 675 of last volume) seemed to yield a starch-product of fine quality, the American method is undoubtedly to be preferred on account of its simplicity. The rice is soaked in caustic soda of 1½° B. for 18 hours, during which time the mixture is occasionally agitated. The liquor is then drawn off and runs out through a long, flat, slightly-inclined shoot, on which a slime containing starch is thus deposited. The residual rice should be soft enough to allow of being easily crushed between the fingers; it is washed repeatedly with water, in order to remove the slime, and then made up into a thin pulp by the addition of a dilute solution of caustic soda. The pulp as it comes from the mill is agitated for about six hours, when the mass is left at rest for 12 hours, which effects a complete separation of the gluten, but at the same time thickens the mass by separating some clear liquor, which is removed by means of a siphon.

The thick pulp is worked through a centrifugal machine, and is thus separated, according to the specific gravity of its ingredients, into three products (1) white raw starch, which is deposited at the sides of the drum, (2) a layer of greyish-white gluten-starch covering the former, and (3) a dirty-yellow alkaline solution of gluten, which may be mixed with the solution used for soaking a fresh quantity of rice. The centrifugal machine is situated on the ground floor of the building, which is divided into three floors. The white, solid raw-starch is taken to the third floor, where it is treated in large vessels with a dilute soda-solution. The starch milk is then passed through a cylindrical sieve, runs into large washing vessels placed on the second floor of the building, and from these it is drawn off into the depositing tanks on the ground floor. The time allowed for depositing is from 24 to 36 hours. After this the liquid is syphoned off, the residue treated with a small quantity of water, and refined by means of centrifugals. For this purpose the author recommends the use of a centrifugal machine, consisting of a cast-iron cylinder 1 m. high and 0.9 m. in diameter, and of a deep copper drum of the shape of a boiler, in the middle of which a copper cone open at the bottom rests on a conical spindle fixed into the middle of the cylinder. The inner walls of the drum are divided into six narrow vertical partitions, and the bottom has two small openings. It is advisable to wash the product again after having expelled the liquor by means of this machine. The washed mass is drained on cloths placed on wooden boxes. The further treatment of the product is similar to that already described, the starch obtained being in rays. The residue left in the washing tanks (second floor) consists principally of gluten starch, cellular tissue, and unground rice-particles. It is treated with water, the mixture passed through a sieve, allowed to ferment, and the separated rice-particles brought back to the mills. The so-called third product left in the centrifugals during their first working has to undergo a similar treatment, while the liquor (caustic soda), which is obtained as filtrate, is used up for soaking a fresh quantity of rice. The fermentation with decomposed wheat-gluten, and the separation of the undissolved substances, is the same as that previously described.

In conclusion, it is noteworthy that the waste liquors resulting from the starch washings still contain a large quantity of starch in suspension, which may be got out by leaving the liquors at rest for some time in large cement reservoirs, when a mass is deposited which is to be treated with water, passed through a sieve, then through a centrifugal machine, treated with a determined quantity of strong sulphurous acid, allowed to settle, washed repeatedly, and finally sifted. In this manner a perfectly pure product is obtained. Instead of sulphurous acid, sulphites of sodium or calcium may be advantageously used. The waste liquor, after having been used for soaking purposes, is treated with hydrochloric acid, which separates the gluten. The separation of gluten may also be effected in a very satisfactory manner by means of magnesium chloride, and it is remarkable that, with the use of a small quantity of this salt, the greater portion of the caustic soda remains unaltered.

D. B. :

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

X.—On High Melting Points, with Special Reference to those of Metallic Salts. Part II.

By THOMAS CARNELLEY, D.Sc. (Lond.), F.C.S., Demonstrator in the Chemical Laboratory of The Owens College.

IN my first paper on this subject (*Chem. Soc. Journ.*, p. 489, April, 1876), I described a method for determining the melting points of bodies which fuse at temperatures too high for a mercurial thermometer to be used. The present communication contains some preliminary experiments with reference to another method I have employed for attaining the same end. This depends on the following principle:—

If three metallic salts, A, B, and C, which fuse at different temperatures, such that A fuses before B, and B before C, be arranged on a cold block of smooth iron, and this be placed in a muffle kept at a constant high temperature, and if x be the number of seconds which elapse between the melting of A and B, and y the number of seconds between the melting of A and C, then the ratio $\frac{y}{x}$ is approximately constant for the same three salts, whatever may be the temperature of the muffle, provided only it is considerably higher than that at which C fuses.

In the present paper I shall give the results of some experiments I have made on this question, and afterwards, in Part III, I propose to describe a method of determining high melting points based on the above principle.

The experiments I am about to detail were originally made solely with the idea of furnishing a further proof as to the correctness of the conclusions arrived at by the specific heat method; but it soon occurred to me that they would lead to a process which might be employed with advantage in actually determining high melting points.

The blocks of metal used were either of steel or of wrought iron, and of the form shown in the accompanying drawings. Figure (1) is a front view of one of these blocks, from which it is seen to be a kind of open oblong box, placed on its side. The salts, whose melting points are to be observed, are arranged on the floor ($a\ b\ c\ d$), at

equal distances apart, and in the positions represented by A, B, and C. In order to prevent the most fusible salt, A, from running when liquified on to B, and also B from coming, on melting, into contact with C, the floor ($a b c d$) slants upward from ($a d$) to ($b c$), so as to form an inclined plane; by this means each salt on fusing tends to run down the plane and not across it, and thus does not interfere with the other two.

Three of these blocks have been used in the experiments given below, which I shall distinguish respectively as Block I (made of steel, weight 850 grams); Block II (of wrought iron, weight 350 grams; and Block III (also of wrought iron, weight 50 grams). Though they differed somewhat in shape, I shall only give details with respect to Block III, since it is the one I have found most convenient, and is that which I have used to determine high melting-points.

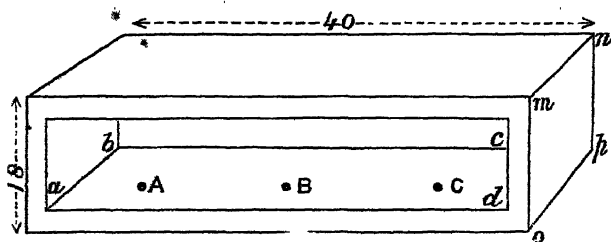


FIG. 1.

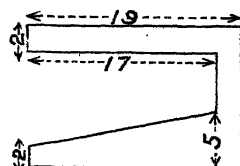


FIG. 2.

These details are clearly shown in figures (1) and (2), where the measurements are given in millimeters, and of which the latter is a section parallel to ($m n o p$). The whole is made out of one piece of metal, with the exception of the end plates ($m n o p$), which are bolted on to the rest; this prevents, to a great extent, the cracking of the block on sudden cooling in water, which would otherwise be very liable to take place were the block to consist of a single piece. By adopting this form of block, the radiation from the sides of the muffle directly on to the salts is obviated as much as possible, so that they are always at the temperature of the metal; while, at the same time, they can be readily seen, and the moment of their melting noted. The iron of which the blocks is made should not froth when raised to a high temperature, or, at any rate, not after having been heated several times.

In the experiments made to prove the constancy of the ratio $\left(\frac{y}{x}\right)$ the three salts, A, B, C, were arranged on the block as described, and the whole was placed in a muffle-furnace kept at a constant

temperature (a Fletcher's gas-muffle was found to answer best, though in some cases a large muffle-furnace, heated by coke, was employed), then, by means of a watch, the exact moment at which each salt melted was observed, and the results so arranged as to show the number of seconds which elapsed between the melting of A and B, and between that of A and C. Let x be the former value and y the latter, then, by repeating the experiment with these same salts at different temperatures of the muffle, it was found that $\left(\frac{y}{x}\right)$ was approxi-

mately constant, whatever that temperature might be, provided only it was considerably above that at which C fuses. After each experiment, the block was cooled in water, and the floor well cleaned by scraping with a knife and rubbing with sand and water; this was especially necessary in the case of insoluble salts, such as lead chloride, silver chloride, &c. Only a very small quantity of each salt (about 0.5 mgrm.) was used in each determination, and as nearly as possible the same corresponding point taken as that at which the salt fuses, since all salts do not melt quite suddenly, the quantity above mentioned often taking three to five seconds. I have found it best always to take, as the true melting point, that at which the *whole* of the small portion of salt became fused. During an observation, the mouth of the muffle was closed by an iron plate, in which there was a small opening sufficiently large to allow of the block and its contents being seen.

Table I, containing 20 series of experiments with different salts, shows some of the results obtained. In the first horizontal line of each series, the letters B¹, B², B³, indicate which of the three blocks mentioned above was used in that particular experiment, and m that the numbers immediately below it were obtained by using a large muffle heated with coke; while, in all other cases, a Fletcher's gas muffle was employed. In the third horizontal line is given the time (x) which elapsed between the melting of the first body and the second, and in the fourth line the time (y) that elapsed between the melting of the first and third, while the fifth line shows the ratio $\left(\frac{y}{x}\right)$.

From the values of (x) given in the third line, an approximate idea may be formed as to the relative temperatures of the muffle in the different experiments, for the higher this temperature was, the less will x be, and *vice versa*.

TABLE I—continued.

XI.	B ³ .	B ³ .	Mean.	XII.	B ³ . m.	B ³ . m.	E ³ .	B ³ . m.	B ³ .	B ³ .	Mean.
S	0	0		S	0	0	0	0	0	0	
KI	128	126		KCl	196	200	204	209	212	237	288
N ₂ O	275	285		N ₂ O	284	270	268	282	269	311	336
Ratio.....	2.24	2.26	2.25	Ratio	1.45	1.35	1.31	1.35	1.27	1.31	1.35

XIII.	B ³ .	B ³ .	Mean.	XIV.	B ³ .	B ³ .	B ³ .	B ³ . m.	B ³ .	B ³ .	B ³ .
S.....	0	0		S.....	0	0	0	0	0	0	
KNO ₃	85	86		KNO ₃	76	80	81	81	83	83	
PbCl ₂	185	191		PbCl ₂	133	134	138	136	136	136	
Ratio.....	2.18	2.22	2.13	Ratio	1.75	1.68	1.70	1.64	1.64	1.69	

XV.	B ³ .	B ³ .	B ³ .	B ³ .	B ³ .	B ³ .	B ³ .	B ³ . m.	B ³ .	B ³ .	B ³ .
AgNO ₃	0	0	0	0	0	0	0	0	0	0	
KNO ₃	52	54	60	67	69	73	128	133	134	145	173
KClO ₃	67	73	75	80	83	84	155	160	164	180	198
Ratio.....	1.29	1.35	1.25	1.23	1.24	1.20	1.21	1.20	1.22	1.24	1.23

TABLE I—*continued*.

XIX.	B ^a .	B ^b .	Mean.	XX.	B ^a .	B ^b .	Mean.
TlCl	0	0		KI	0	0	
KCl	185	140		KCl	76	86	
Na ₂ CO ₃	198	204		Na ₂ CO ₃	146	164	
Ratio	1·47	1·46	1·46	Ratio	1·92	1·91	1·91

An inspection of this table shows that the ratio $\left(\frac{y}{x}\right)$ is approximately constant, and in several of the series, extending over a wide range of temperature, it is almost quite constant. Only those values of $\left(\frac{y}{x}\right)$, however, are strictly comparable, which were obtained by using the same block, but nevertheless in almost all, whatever the size of the block, the ratio is as nearly constant as could have been expected from the nature of the case; those got by means of Block II are, however, as a rule, somewhat higher than the others. The numbers given in the columns headed by *m*, can be considered as only fairly approximate, since it was difficult, if not impossible, to keep a large muffle heated by coke for any length of time at a constant high temperature. Even in those series in which the ratio appears to vary somewhat considerably, it is quite evident, on comparing the values given, that this variation does not depend on the temperature of the muffle, except, perhaps, in the case of sodium carbonate and potassium chloride, which fuse at a pretty high temperature, and therefore approached too nearly to that of the furnace. It is probable that these variations are due to errors of experiment, since it is difficult, as already mentioned, always to hit exactly the right melting point in every case, and the time, too, cannot be noted correctly to within one or even two seconds.

The following table gives a comprehensive view of the mean ratios obtained in Table I, together with a number of others, for different salts not shown in the latter. The two salts placed at the head of each column are the first two of each set, while the third is given in the first column; thus the ratio of the three bodies—sulphur, lead-chloride, and potassium chloride, is 3·33, and that of sulphur, potassium chlorate, and lead-chloride 1·78.

TABLE

	S. Na ₂ CO ₃	S. KCl	S. KI	S. PbCl ₂	S. TlCl	S. Zn KClO ₃	S. KNO ₃	S. AgNO ₃	KNO ₃ KNO ₃	KClO ₃ Na ₂ CO ₃	KClO ₃ KCl	KClO ₃ KI	PbCl ₂ KClO ₃	TlCl KClO ₃	KClO ₃ TlCl	TlCl KCl	TlCl PbCl ₂	PbCl ₂ KCl	PbCl ₂ KI
KNO ₃ ..	—	.13	.21	.46	.59	.85	1.00	2.72	—	—	—	—	—	—	—	—	—	—	—
KClO ₃ ..	.13	.16	.28	.56	.71	1.00	1.17	—	1.00	—	—	—	—	—	—	—	—	—	—
TlCl18	.24	.40	.79	1.00	1.40	1.69	—	3.94	.056	.08	.16	.48	1.00	1.00	—	—	—	—
PbCl ₂ ..	.24	.30	.54	1.00	1.27	1.78	2.18	—	6.18	.12	.16	.33	1.00	2.04	2.04	—	1.00	—	—
KI44	.59	1.00	1.86	2.52	3.57	4.65	—	—	.40	.53	1.00	3.06	6.05	6.05	—	5.67	.39	1.00
KCl74	1.00	1.70	3.33	4.22	6.21	7.75	—	—	.73	1.00	1.92	6.15	12.71	12.71	1.00	—	1.00	2.54
Na ₂ CO ₃ ..	1.00	1.35	2.25	4.09	5.02	7.91	—	—	—	1.00	1.37	2.48	8.63	17.80	17.80	1.46	—	1.50	3.49

TABLE III.

	S. Na ₂ CO ₃	S. KOL	S. KI	S. PbCl ₂	S. TlCl	S. KClO ₃	S. KNO ₃	KNO ₃	KClO ₃ / Na ₂ CO ₃	KClO ₃ / KOL	KClO ₃ / KI	KClO ₃ / PbCl ₂	KClO ₃ / TlCl	TlCl/ KCl	TlCl/ PbCl ₂	PbCl ₂ / KCl	PbCl ₂ / KI
KNO ₃	—	·96	·90	1·00	1·00	1·00	1·00	—	—	—	—	—	—	—	—	—	—
KClO ₄	1·22	1·18	1·20	1·22	1·20	1·18	1·17	1·20	—	—	—	—	—	—	—	—	—
TlCl.....	1·69	1·77	1·71	1·72	1·69	1·66	1·69	1·71	1·67	1·70	1·70	1·70	1·70	—	—	—	—
PbCl ₂	2·25	2·21	2·31	2·17	2·15	2·09	2·18	2·10	2·20	2·21	2·23	2·21	2·21	—	2·20	—	—
KI.....	4·18	4·35	4·29	4·32	4·27	4·20	4·65	—	4·52	4·53	4·30	4·21	4·13	—	4·38	4·20	4·30
KCl.....	6·94	7·37	7·29	7·24	7·15	7·31	7·75	—	7·26	7·49	7·09	7·20	7·38	7·29	—	7·32	7·34
Na ₂ CO ₃	9·39	9·96	9·64	8·89	9·53	9·31	—	—	9·51	9·31	8·69	9·59	9·86	9·85	—	9·87	9·22

In order to compare together the ratios obtained with different salts, they must all be reduced to the same scale. Thus, if $\cdot 13$ in the second column be increased to $0\cdot 96$, and all the numbers in that column in the same proportion, and likewise with the other first eight columns, numbers are obtained which, in the same horizontal line, are almost identical. By calculations differing somewhat from those in the case of the first eight, the ratios given in the remaining columns may be reduced to values (reckoning from sulphur) which, on the same horizontal lines, are nearly identical with each other and with those in the preceding eight columns. This is seen in Table III, p. 375, which shows that reckoning from sulphur, the same value is obtained for the salts given in the first column, whatever the salts placed at the heads of the succeeding columns may be, provided we always represent the ratio between sulphur and potassium nitrate and any other third salt by one and the same number.

From these results and those given in Table I, it follows that the principle stated in the beginning of this paper is true, and borne out by experiment.

It is scarcely necessary to remark that these numbers really refer to the rise of temperature of the block itself, the salts being merely used to indicate when the metal had attained a certain temperature.

The meaning of the approximate identity of the numbers in the same horizontal lines of the above table, will be seen from what is given in Part III, in which I propose to show how this time-principle may be employed in the determination of high melting points.

Part III. *A "Time Method" for the Determination of High Melting Points.*

In Part II, I have proved that the ratio between the differences of the times of melting of any three given salts remains approximately constant, whatever may be the temperature of the surrounding envelope. I shall now proceed to show what service this principle renders in the determination of high melting points by a process which I shall term the "Time Method," in order to distinguish it from the "Specific-heat Method" described in a former communication. It is not, however, a perfectly independent one, but presupposes that the melting points of a small number of salts are already known, and these salts I shall call "Standard Salts." They are nine in number, viz., sulphur, silver nitrate, potassium nitrate, potassium chlorate, thallium chloride, lead chloride, potassium iodide, potassium chloride, and sodium carbonate. The melting points which I have assigned to these bodies are those which have been obtained by means of the specific-heat process.

In what follows I shall give (1.) The determination of the "time values" of these nine standard salts. (2.) A description of the "time method" for determining high melting points and results obtained by it. (3.) An account of the service which it renders in favour of the correctness of the results obtained by the specific-heat method.

§ 1. *Determination of the Time Values of Nine Standard Salts.*

By the "time value" of a salt I mean the time which elapses between the fusing of that salt and of sulphur, when, under the same conditions, ten seconds elapse between the melting of sulphur and of silver nitrate.

The following example will make this clear:—

In a number of experiments the results given below were obtained, when the three bodies, sulphur, silver nitrate, and potassium nitrate, were placed on one of the blocks mentioned in Part II, and their times of melting above that of sulphur noted.

S	0	0	0	0
AgNO ₃	27	39	45	65
KNO ₃	72	106	120	170

Here it is seen that the time which elapsed between the melting of sulphur and of silver nitrate varied in each case. Let us suppose, however, that it was the same in every instance, viz., ten seconds, then the time between the melting of sulphur and of nitre will be constant also. For if in the first case 72 seconds elapse between sulphur and nitre, when there are 27 between sulphur and silver nitrate, then there will, by a simple proportion, be 26·7 seconds between sulphur and nitre, when there are 10 seconds between sulphur and silver nitrate. If this calculation be made in every case, almost exactly the same number is obtained for the time which elapses between sulphur and nitre, thus:—

S	0	0	0	0
AgNO ₃	10	10	10	10
KNO ₃	26·7	27·2	26·7	26·7

That this should be so follows from the principle stated in Part II. The mean of a large number of experiments (from which the four given above have been selected) shows that 26·8 seconds elapse between the melting of sulphur and of nitre, when 10 seconds elapse between the melting of sulphur and of silver nitrate. This number, 26·8, is then the "time value" of potassium nitrate.

Again, the following are some of the experimental numbers obtained for sulphur, potassium nitrate, and potassium chlorate :—

S	0	0	0
KNO ₃	29	41	51
KClO ₃	34	47	59

If now in each of these cases the time between sulphur and nitre be represented by the number obtained above, viz., 26·8, we obtain the following, the figures in the third line being almost constant :—

S	0	0	0
KNO ₃	26·8	26·8	26·8
KClO ₃	31·4	30·7	31·0

The mean of a number of experiments yields 31·0 as the time in seconds which elapse between sulphur and potassium chlorate, when 26·8 elapse between sulphur and potassium nitrate, or 10 between sulphur and silver nitrate. This number 31, then, is the time value of potassium chlorate.

As a last and more complicated case, I will give the following, with the three salts, nitre, potassium chlorate, and thallium chloride :

KNO ₃	0	0	0
KClO ₃	8	10	11
TlCl	34	41	47

If in the above the times be reckoned from 26·8, the time value of nitre, instead of from zero, and if the time between nitre and potassium chlorate be taken as constant in each case, viz., 4·2, then the following numbers are obtained :—

KNO ₃	26·8	26·8	26·8
KClO ₃	31·0	31·0	31·0
TlCl	44·6	44·0	44·7

In a similar manner from a series of experiments the mean value, 44, was obtained for the time which elapses between the melting of sulphur and of thallium chloride; 44 is, therefore, the time value of the latter. By proceeding in this way almost the same time values are arrived at for a given salt, whatever the other two salts used to obtain it may be, provided the values attached to them are on the same scale as that which represents the time between sulphur and silver nitrate as 10 seconds.

TABLE

	S.	Na ₂ CO ₃	KOL	KI.	PbCl ₂	TIOL	S.	KClO ₃	S.	KNO ₃	S.	AgNO ₃	AgNO ₃	KNO ₃	KClO ₃	Na ₂ CO ₃	KClO ₃	KOL	KClO ₃	KI.	KClO ₃	PbCl ₂	KClO ₃	TIOL	TIOL	PbCl ₂	KOL	PbCl ₂	Mean.
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AgNO ₃ ..	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
KNO ₃	—	—	26	24	27	27	27	27	27	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
KClO ₃	34	34	32	32	32	32	32	32	32	31	31	—	—	32	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
TIOL	46	46	48	46	46	46	46	46	46	—	—	—	—	47	45	45	45	45	45	45	45	44	44	46	—	—	—	—	—
PbCl ₂	62	62	59	62	58	58	58	57	59	—	—	—	—	58	59	59	59	59	59	59	59	58	58	61	58	—	—	—	—
KI	114	114	117	115	107	116	116	114	125	—	—	—	—	—	122	120	115	115	115	115	115	112	117	117	114	114	115	115	115
KOL	191	191	198	195	193	194	194	199	209	—	—	—	—	—	197	198	191	191	198	198	198	192	210	210	—	—	203	203	203
Na ₂ CO ₃ ..	258	258	267	259	237	258	258	253	—	—	—	—	—	—	258	259	238	256	268	268	268	256	281	281	—	—	257	257	258

The time value of any salt may also be derived from the ratios given in Table II, Part II, by using the equation $\left(\frac{y}{x} = r\right)$ where x and y have the signification there attached to them, r being the experimental ratio given in the table above mentioned. Thus, on referring to that table we find that the value of r for sulphur, silver nitrate, and potassium chlorate = 2.72: therefore in this case $\frac{y}{x} = 2.72$; and if $x = 10$, then $y = 27.2$, which is the time value of potassium nitrate.

Again, the value of r for the three salts, lead chloride, potassium chloride, and sodium carbonate, is found from the table to be 1.50, therefore $\frac{y}{x} = 1.50$. Now, if the time values of lead chloride and potassium chloride be 59 and 197 respectively (these numbers being found by previous experiment), then $x = 138$, and, therefore, $y = (1.50 \times 138) = 207$, or sodium carbonate melts 207 seconds after lead chloride; and since the latter melts 56 seconds after sulphur, therefore the time value of sodium carbonate = $(207 + 59) = 266$ seconds.

If all the ratios given in Table II, Part II, be thus converted into time values, we obtain the numbers which are represented in Table I (p. 379):—

As will be seen from this table, almost the same time value is obtained for a given salt, whatever the other two salts used may be. But the table shows also that the higher the melting point of the salt the greater is the difference between these values; this, however, could only be expected from the nature of the case, since the higher the melting point the nearer does it approach to the temperature of the muffle, and therefore the ratio $\left(\frac{y}{x}\right)$ does not strictly hold when that melting point becomes pretty high.

The nature of the other two salts employed appears to have no influence on the result at all, or at any rate it cannot be detected in the table.

The numbers given above are the mean results obtained with the three different blocks mentioned in Part II. I have thought it best, however, in the experiments in paragraphs 3 and 4, to make use of those time values only which have been arrived at by employing the same block as that used in making these experiments. They are as follows, the second column giving the corresponding melting points:—

TABLE II.*

Salt.	M. P.	Time value.
S	118	0
AgNO ₃	233	10
KNO ₃	368	26.8
KClO ₃	388	31
TlCl.....	453	44
PbCl ₂	524	56
KI	668	108
KCl.....	770	180
Na ₂ CO ₃	854	241

If now in the above table the melting points of the different salts be made to represent the abscissæ, and the time values the ordinates, a curve (A) similar to that shown in Figure I is obtained.

By interpolation the table given below has been constructed, in which the columns headed I give the time values, and those marked II the corresponding melting points.

TABLE III.

I.	II.	I.	II.	I.	II.	I.	II.
0	118	21	320	42	443	63	552
1	122	22	328	43	448	64	555
2	140	23	337	44	453	65	559
3	151	24	345	45	460	66	563
4	163	25	353	46	466	67	566
5	174	26	362	47	472	68	570
6	185	27	370	48	478	69	574
7	196	28	374	49	484	70	578
8	208	29	378	50	490	71	584
9	221	30	382	51	496	72	587
10	233	31	388	52	501	73	591
11	241	32	393	53	507	74	594
12	249	33	398	54	512	75	598
13	257	34	403	55	518	76	601
14	265	35	408	56	524	77	604
15	273	36	413	57	529	78	608
16	281	37	418	58	533	79	611
17	289	38	423	59	538	80	614
18	297	39	428	60	541	81	617
19	304	40	433	61	545	82	619
20	311	41	438	62	548	83	622

* The melting points in this table are a few degrees higher than those given in Part I, owing to an error having been discovered (subsequently to the publication of that paper) in the value of the calorimeter there employed.

TABLE III—*continued*.

I.	II.	I.	II.	I.	II.	I.	II.
84	624	124	691	164	749	208	808
85	627	125	693	165	750	204	805
86	629	126	694	166	752	205	806
87	632	127	696	167	753	206	808
88	634	128	697	168	755	207	809
89	637	129	699	169	757	208	811
90	639	130	700	170	758	209	812
91	641	131	702	171	760	210	813
92	642	132	703	172	761	211	815
93	644	133	705	173	762	212	816
94	646	134	706	174	763	213	817
95	648	135	707	175	765	214	819
96	649	136	709	176	766	215	820
97	650	137	710	177	767	216	821
98	652	138	712	178	768	217	823
99	654	139	713	179	769	218	824
100	656	140	714	180	770	219	825
101	658	141	716	181	772	220	826
102	659	142	717	182	773	221	828
103	661	143	719	183	775	222	829
104	662	144	721	184	776	223	830
105	664	145	722	185	777	224	832
106	665	146	724	186	779	225	833
107	667	147	725	187	780	226	835
108	668	148	726	188	782	227	836
109	670	149	727	189	784	228	837
110	671	150	728	190	785	229	839
111	673	151	730	191	787	230	840
112	674	152	731	192	788	231	841
113	676	153	733	193	789	232	843
114	677	154	734	194	791	233	844
115	679	155	735	195	792	234	846
116	680	156	737	196	793	235	847
117	681	157	738	197	795	236	848
118	683	158	740	198	796	237	850
119	684	159	741	199	798	238	851
120	685	160	743	200	799	239	852
121	687	161	745	201	801	240	853
122	688	162	746	202	802	241	854
123	690	163	748				

§ 2. *A Description of the Time Method for Determining High Melting Points and Results.*

For this purpose the time value of the salt, whose melting point is required, is found experimentally, and then by referring to Table III, we discover the corresponding melting point.

In order to determine the time value, the given salt was placed together with two of the standard salts on block III, heated in the muffle, and the times of melting noted in the manner already described.

From the numbers so obtained the time value can be calculated just as in the case of the standard salts themselves.

The following table represents the results arrived at by this method in the case of thirteen different salts. Under each salt is given in the first column the standard salts used, and in the horizontal lines headed "T.V." the time values found by experiment, while in those headed "M.P." are shown the melting points corresponding to these values as found by referring to Table III.

TABLE IV.—*Mercuric Chloride.*

Standard Salts.						Mean.
S and KClO_3	{ T. V.	22	22	19	20	21
	{ M. P.	328	328	304	311	320
S and TiCl	{ T. V.	20	22	—	—	21
	{ M. P.	311	328	—	—	320
				Mean { T. V.		21
					{ M. P.	320

Sodium Nitrate.

S and KClO_3	{ T. V.	23	25	25	23	24
	{ M. P.	337	353	353	337	345
S and TiCl	{ T. V.	21	24	23	24	23
	{ M. P.	320	345	337	345	337
S and KNO_3	{ T. V.	22	24	24	24	24
	{ M. P.	328	345	345	345	345
				Mean { T. V.		24
					{ M. P. ..	345

Silver Bromide.

S and PbCl_2	{ T. V.	46	47	46	—	46
	{ M. P.	466	472	466	—	466
S and KClO_3	{ T. V.	45	44	44	—	44
	{ M. P.	460	453	453	—	453
KClO_3 and PbCl_2 .	{ T. V.	44	42	—	—	43
	{ M. P.	453	448	—	—	448
				Mean { T. V.		44
					{ M. P. ..	453

Thallium Iodide.

S and PbCl_2	{ T. V.	48	49	45	46	47
	{ M. P.	478	484	460	466	472
S and KClO_3	{ T. V.	46	45	47	—	46
	{ M. P.	466	460	472	—	466
KClO_3 and PbCl_2 .	{ T. V.	49	44	47	48	47
	{ M. P.	484	453	472	478	472
				Mean { T. V.		47
					{ M. P. ..	472

Silver Chloride.

Standard Salts.						Mean.
S and PbCl_2	{ T. V.	50	52	51	—	51
	{ M. P.	490	501	496	—	496
S and KClO_3	{ T. V.	49	48	51	—	49
	{ M. P.	484	478	496	—	484
KClO_3 and PbCl_2	{ T. V.	52	51	49	51	51
	{ M. P.	501	496	484	496	496
				Mean { T. V.	50	50
				{ M. P. ...	490	490

Silver Iodide.

S and PbCl_2	{ T. V.	75	77	—	—	76
	{ M. P.	598	604	—	—	601
S and TiCl_3	{ T. V.	67	69	—	—	68
	{ M. P.	566	574	—	—	570
TiCl_3 and PbCl_2 ..	{ T. V.	76	76	—	—	76
	{ M. P.	601	601	—	—	601
				Mean { T. V.	73	73
				{ M. P. ...	591	591

Sodium Iodide.

S and KCl	{ T. V.	103	96	91	102	98
	{ M. P.	661	649	641	659	652
S and PbCl_2	{ T. V.	98	101	86	103	97
	{ M. P.	652	658	629	661	650
KClO_3 and PbCl_2	{ T. V.	100	111	96	—	102
	{ M. P.	656	673	649	—	659
				Mean { T. V.	99	99
				{ M. P.	654	654

Calcium Bromide.

S and KCl	{ T. V.	132	129	—	—	131
	{ M. P.	703	699	—	—	702
S and KI	{ T. V.	129	133	—	—	131
	{ M. P.	699	705	—	—	702
KClO_3 and PbCl_2	{ T. V.	154	140	136	—	143
	{ M. P.	734	714	709	—	719
				Mean { T. V. ...	135	135
				{ M. P. ...	707	707

Lithium Carbonate.

S and KCl	{ T. V.	125	122	—	—	124
	{ M. P.	693	688	—	—	691
S and KI	{ T. V.	155	144	132	149	145
	{ M. P.	735	721	703	727	722
PbCl_2 and KCl ..	{ T. V.	124	113	—	—	119
	{ M. P.	691	676	—	—	684
				Mean { T. V. ...	129	129
				{ M. P. ...	690	690

Potassium Bromide.

Standard Salts.						Mean.
S and KCl	{ T. V.	144	142	142	—	143
	{ M. P.	721	717	717	—	719
S and KI	{ T. V.	155	149	—	—	152
	{ M. P.	735	727	—	—	731
KClO ₃ and PbCl ₂	{ T. V.	170	161	—	—	165
	{ M. P.	758	745	—	—	750
	Mean { T. V. ..					153
	{ M. P. ..					733

Sodium Bromide.

S and KCl	{ T. V.	150	150	145	—	148
	{ M. P.	728	728	722	—	726
S and PbCl ₂	{ T. V.	160	157	160	—	159
	{ M. P.	743	738	743	—	741
KI and KCl	{ T. V.	151	149	148	—	149
	{ M. P.	730	727	726	—	727
	Mean { T. V. ..					152
	{ M. P. ..					731

Calcium Chloride.

S and PbCl ₂	{ T. V.	158	160	—	—	159
	{ M. P.	740	743	—	—	741
S and KI	{ T. V.	162	163	—	—	163
	{ M. P.	746	748	—	—	748
KI and KCl	{ T. V.	161	158	—	—	160
	{ M. P.	745	740	—	—	743
	Mean { T. V. ..					161
	{ M. P. ..					745

Sodium Chloride.

S and KI	{ T. V.	196	196	—	—	196
	{ M. P.	793	793	—	—	793
S and PbCl ₂	{ T. V.	226	215	213	—	218
	{ M. P.	835	820	817	—	824
KI and KCl	{ T. V.	217	224	—	—	220
	{ M. P.	823	832	—	—	826
	Mean { T. V. ...					211
	{ M. P. ...					815

These results may be compared more easily in the following table, in which the salts whose melting points have been determined by this method are shown in the first column, while the standard salts employed are placed at the heads of the succeeding columns:—

TABLE V.

Salt.		S. KNO ₃	S. KClO ₃	S. TiCl ₃	S. PbCl ₃	S. KI.	S. KCl.	KClO ₃ PbCl ₃	TiCl. PbCl ₃	PbCl ₂ KCl.	Kl. KCl.	Mean.
HgCl ₂	{ T. V. M. P.	21 320	21 320	21 320	—	—	—	—	—	—	—	21 320
NaNO ₃	{ T. V. M. P.	24 345	24 345	23 337	—	—	—	—	—	—	—	24 345
AgBr	{ T. V. M. P.	44 453	46 466	—	46 466	—	—	43 448	—	—	—	44 453
TlI	{ T. V. M. P.	46 466	47 472	—	47 472	—	—	47 472	—	—	—	47 472
AgCl	{ T. V. M. P.	49 484	51 496	—	51 496	—	—	51 496	—	—	—	50 490
AgI	{ T. V. M. P.	—	76 601	68 570	76 601	—	—	—	76 601	—	—	73 581
NaI	{ T. V. M. P.	—	97 650	—	97 650	—	98 652	102 659	—	—	—	99 654
CaBr ₂	{ T. V. M. P.	—	—	—	—	131 702	131 702	143 719	—	—	—	135 707
Li ₂ CO ₃	{ T. V. M. P.	—	—	—	—	145 722	145 722	124 691	—	119 684	—	129 699
KBr	{ T. V. M. P.	—	—	—	—	152 731	143 719	165 750	—	—	—	153 733
NaBr	{ T. V. M. P.	—	159 741	—	159 741	—	143 726	—	—	—	149 727	152 731
CaOCl ₂	{ T. V. M. P.	—	—	—	159 741	163 748	—	—	—	—	160 745	161 745
NaCl	{ T. V. M. P.	—	—	—	218 824	196 793	—	—	—	—	220 826	211 815

In Table VI are given the values obtained by the "time" and "specific heat" methods respectively, from which it is seen that almost the same mean melting points result from both.

TABLE VI.

Salt.	HgCl ₂ .	NaNO ₃ .	AgBr.	TlI.	AgCl.	AgI.	NaI.	CaBr ₂ .	Li ₂ CO ₃ .	KBr.	NaBr.	CaCl ₂ .	NaCl.
Time method ..	320	345	453	472	490	591	654	707	699	733	731	745	815
Specific heat method }	315	345	453	466	477	554	661	710	729	733	742	753	811
Difference	+5	0	0	+6	+13	+37	-7	-3	-30	0	-11	-8	+4

Of the two methods, I consider the one depending on specific heats to be the more accurate, since the results obtained by it for the same salt agree more nearly among themselves than do those arrived at by the time method, while the exact point at which the salt melts is more easily seen in the case of the former. The same method, too, is to be especially preferred, because it is entirely *independent of any fixed melting points*; whereas, in the time method, the melting points of the standard salts, as found by the other method, have to be assumed, so that the results which it yields are not wholly independent ones.

§ (3.) *Service rendered by the Time Method in favour of the Correctness of the Results obtained by the Specific Heat Method.*

In my first paper on the subject of high melting points, I mentioned that the results there obtained did not, especially in the case of those salts which fuse above 800° C., agree at all well with those given by Braun in his paper on "The Electric Conductivity of Fused Salts." This being the case, any point which bears at all on the question in favour of either the one or the other of these two sets of values is of importance, and such is offered by the results yielded by the time method; for though the actual melting points obtained by it are not entirely independent ones, yet the time values of the salts are. So that, if two curves be constructed in which the same time values are represented by the abscissæ of both, while the ordinates of each curve respectively represent the corresponding melting points as found by the specific heat method and by Braun, then they will have the form shown in Figure I, where the continuous line (A) is that got

from the specific heat results, and the dotted one (B), that from Braun's numbers. From this, it will be seen that the former curve is almost quite regular, while the latter is somewhat irregular, which, it may safely be said, would not be the case were Braun's melting points correct. It is irregular, too, in a way which shows that at least some of his melting points cannot be true, for Braun's curve (B) first rises gradually from 100° C. to 580°, and then turns somewhat suddenly upwards, continuing to be rather steep up to 730°, at which point it again turns and becomes much less so. Now this is contrary to what such a curve ought to be, for the higher the melting point, the steeper the curve should become, i.e., the more rapidly ought the time values to increase, because the temperature of the surrounding envelope is the more nearly approached. On the other hand, the curve derived from the melting points obtained by the specific heat method is perfectly in accord with this principle.

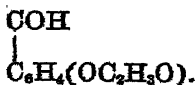
XI.—*On the Formation of Coumarin and of Cinnamic and of other Analogous Acids from the Aromatic Aldehydes.*

By W. H. PERKIN, F.R.S.

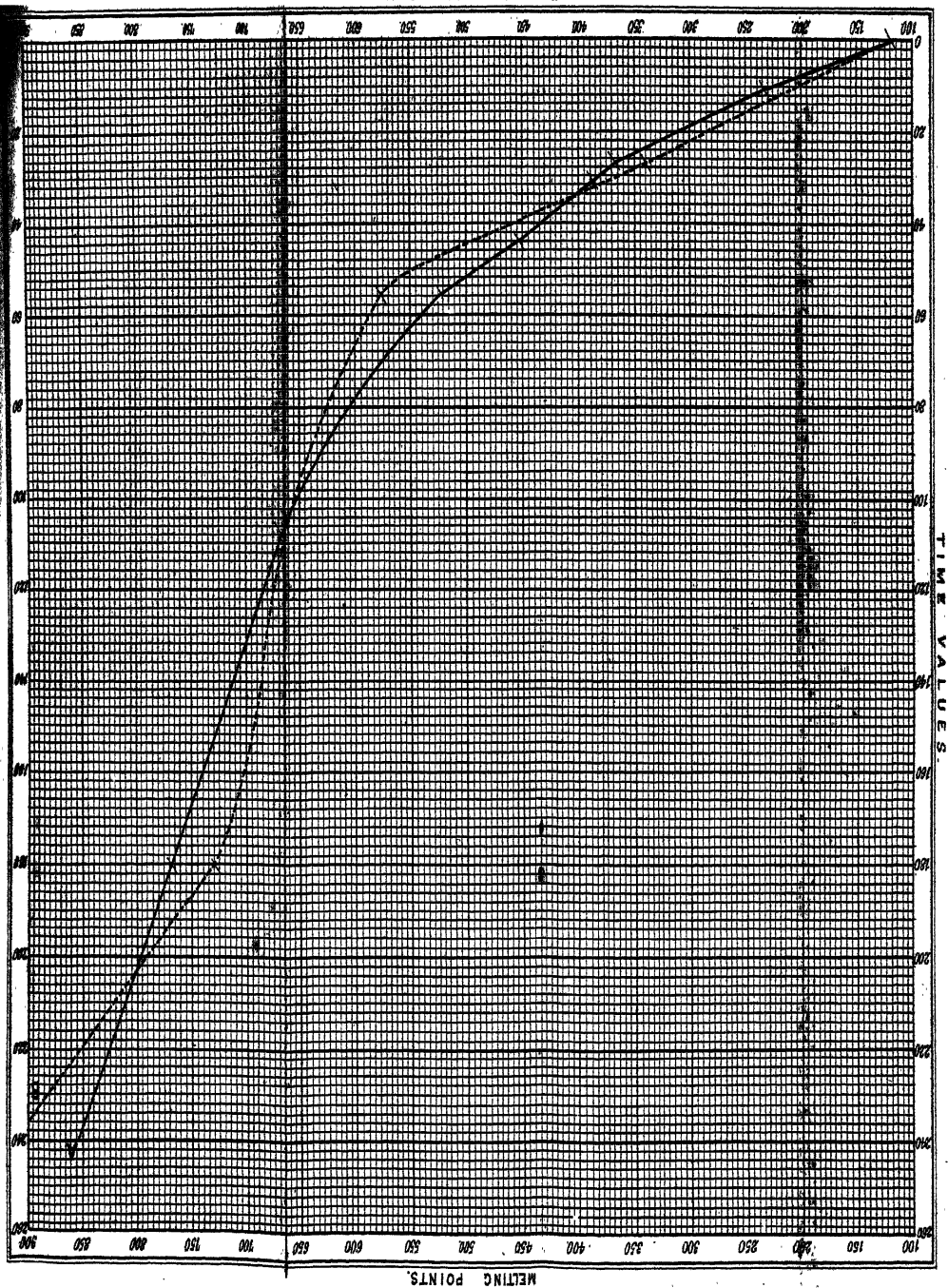
IN November, 1875 (*Chem. News*, vol. xxxii, p. 258), I brought before the Society a short preliminary account of the experiments on this subject in which I was then engaged. Since then I have been further working in the same direction, and will now give an account of my results up to the present time.

These experiments were at first commenced with the hope of obtaining some light upon the peculiar reactions by which the coumarins are formed. It will be remembered that in the process by which I succeeded in preparing these bodies, the products employed were the sodium-derivative of the hydride of salicyl and the anhydrides of the fatty acids (*Journ. Chem. Soc.*, xxi, 53).

It is known that when acetic anhydride acts upon the sodium-compound of the hydride of salicyl, acetate of sodium and hydride of aceto-salicyl are produced (*Journ. Chem. Soc.*, xxi, 181), the former having the composition—



The phenolic hydrogen of the aldehyde having been thus replaced



by acetyl, this substance would consequently have the properties of an ordinary aldehyde.

This being the case, it appeared probable that the next part of the reaction in the formation of coumarin took place between the aldehydic group, the sodium acetate, and the acetic anhydride, the resulting product then splitting up into acetic acid and coumarin.

It was obvious that neither the hydride of aceto-salicyl nor the hydride of salicyl would yield coumarin if heated with acetic anhydride *only*, as they are known to form other compounds with this substance. (*Journ. Chem. Soc.*, xxi, 183, and xx, 587.)

A quantity of hydride of salicyl was, therefore, boiled with acetic anhydride and sodium acetate, and then treated as described in my paper already referred to, when, to my surprise, I found that coumarin had been produced in quantity.

Thinking it unlikely that the sodium of the acetate used could have replaced the phenolic hydrogen of the salicylic aldehyde and thus have influenced the reaction, I was induced to try similar experiments with other aromatic aldehydes, the first I selected being benzoic aldehyde.

ACIDS FROM BENZOIC ALDEHYDE.

I.—*Cinnamic Acid.*

On boiling this aldehyde with acetic anhydride and sodium acetate, chemical action took place, but much more slowly than when hydride of salicyl was employed; nevertheless, after heating the mixture for about a day, a good deal of change was found to have taken place, and on separating the sodium acetate with water, and treating the oily residue with an alkaline carbonate, a considerable quantity of an organic acid dissolved, which, when precipitated by an acid and purified by crystallisation from dilute spirit, was found to be pure cinnamic acid. Similar operations were then made in sealed tubes, a temperature of about 180° C. being employed and continued for five or six hours. On opening the tubes, carbonic anhydride escaped,* and on examining the solid crystalline mass, it was found to contain cinnamic acid in large quantities; in some experiments as much as 84 per cent. of acid has been obtained from the benzoic aldehyde employed.

To procure the cinnamic acid in the pure state by this process,

* The formation of carbonic anhydride in this and in the other analogous operations described in this paper is believed to be due to the decomposition of the organic acid by heat, this gas and a hydrocarbon resulting, which in this case would be cinnamene.

I have found it convenient first to boil the product of the reaction with water in a retort; by this means, any unconverted aldehyde is separated, being carried over by the steam. The residue is then allowed to cool, during which time the crude oily cinnamic acid solidifies, and any dissolved in the aqueous saline solution crystallises out. It is then collected on a filter, washed from sodium acetate, boiled with sodium carbonate, and after cooling, filtered from the oily impurities which are always present. On acidifying the alkaline solution, the cinnamic acid separates as a white pasty crystalline precipitate; this is further purified by two or three crystallisations from dilute alcohol.

Experiments have been made in which the sodium acetate has been replaced by other salts, such as sodium valerate, and also by lead acetate, but in all cases cinnamic acid resulted, the formation of the acid being apparently due to the anhydride employed, and not to the acid of the salt used.

The following are the results of the analysis of the cinnamic acid obtained by these methods:—

- I. .2465 of substance gave
 .657 of CO_2 and
 .122 of H_2O .
- II. .264 of substance gave
 .7013 of CO_2 and
 .1322 of H_2O .
- III. .244 of substance gave
 .6535 of CO_2 and
 .118 of H_2O .
- IV. .3684 of substance gave
 .9815 of CO_2 and
 .184 of H_2O .

Theory for $\text{C}_9\text{H}_8\text{O}_2$.		Experiment.			
		I.	II.	III.	IV.
Carbon	72.97	72.70	72.88	73.04	72.73
Hydrogen	5.47	5.49	5.60	5.40	5.54

The substance employed for No. I was prepared with sodium acetate and acetic anhydride. In Nos. II and III, the sodium acetate was replaced by sodium valerate, and in No. IV by sodium butyrate.

The proportions I have generally employed are one of sodium salt, two of aldehyde, and three of anhydride. The amount of sodium salt is important. I have found that by reducing it to about a fourth part of the aldehyde used, that only 50 per cent. of cinnamic acid was obtained; but when it was increased to the same weight as the aldehyde, the yield was not greater than when half that quantity was used.

The product found in the sealed tubes after heating, is a clear pale-brown fluid which, on cooling, becomes a solid or semi-solid crystalline mass, through which small pale-coloured opaque nodules separate; more particularly when sodium valerate is used in place of acetate. Some of these were separated by the addition of acetic anhydride, which dissolves out the crystalline substance consisting apparently of the compound of sodium acetate and acetic anhydride. After being further washed with fresh anhydride, the product, consisting of these opaque masses, was obtained moderately pure. It was freed from anhydride under a bell-jar over potassium hydrate, and then at 100° .

This substance, when treated with water, decomposes, yielding cinnamic acid and sodium cinnamate. It dissolves in strong aqueous ammonia without forming cinnamide. On analysis, it gave the following numbers:—

- I. .317 of substance gave
 .070 of Na_2SO_4 = 7.12 per cent. sodium.
- II. .456 of substance gave
 .102 of Na_2SO_4 = 7.24 per cent. sodium.

From these results the product is undoubtedly a compound of sodium cinnamate with cinnamic acid, $\text{C}_9\text{H}_7\text{NaO}_2, \text{C}_9\text{H}_5\text{O}_2$ (which requires 7.2 per cent. sodium), corresponding to the already known acid potassium benzoate, $\text{C}_7\text{H}_5\text{KO}_2, \text{C}_7\text{H}_5\text{O}_2$.

II.—*Phenylcrotonic Acid.*

Cinnamic acid having been so easily produced by the process just described, I naturally made further experiments in this direction, substituting other anhydrides for acetic. The following results were obtained when propionic anhydride was employed.

Sealed tubes were charged with one part of sodium propionate, two parts of benzoic aldehyde, and three parts of propionic anhydride, and then heated to 180° for six or seven hours; the tubes, on cooling, contained a nearly solid mass, consisting of two kinds of crystals moistened with an oily product. On opening the tubes, carbonic anhydride escaped.

The product of this reaction was mixed with water and boiled in a retort until oily matter nearly ceased to distil off. The residue was left for some time until quite cold, and then thrown on a filter and washed with cold water to remove sodium propionate. It was then boiled with a solution of sodium carbonate, filtered from a small quantity of neutral oil, and treated with ether to remove the last traces of this product. The clear alkaline solution was afterwards heated, and acidified with hydrochloric acid, which caused a copious white precipitate to separate. When cold, this was collected on a filter, washed

with cold water, and then twice crystallised from alcohol, after which it was submitted to analysis.

- I. .268 of substance gave
 .7257 of CO_2 and
 .151 of H_2O .
 II. .2785 of substance gave
 .757 of CO_2 and
 .155 of H_2O .

	Theory for $\text{C}_{10}\text{H}_{10}\text{O}_2$.	Experiment.	
		I.	II.
Carbon	74.07	73.85	74.12
Hydrogen	6.17	6.33	6.19

This acid is, therefore, phenyl-crotonic acid—



In one operation, sodium acetate was employed in place of sodium propionate, but the same result was obtained.

Phenylcrotonic acid melts at 82° to a clear oil, but as the temperature falls, it becomes a beautifully crystalline mass. It is easily soluble in alcohol, especially when hot, from which it separates as the solution cools in transparent oblique crystals. It is also slightly soluble in boiling water, and crystallises from it on cooling in fine needles.

Barium salt, $\text{C}_{20}\text{H}_{18}\text{BaO}_4\text{Aq}$. When boiled with a solution of barium hydrate the acid dissolves, and on cooling deposits this salt in beautiful fern-like crystals; these were collected, washed, and recrystallised. It is a beautifully white salt, and when examined by the lens, the crystals appear to be plates. Cold water dissolves it to a small extent only. The crystals become opaque when dried in the water-oven, from loss of water of crystallisation. It gave the following numbers on analysis. The combustions were made with lead chromate:—

- I. .2805 of substance dried at 150°C . gave
 .535 of CO_2 and
 .1047 of H_2O .
 II. .1408 of substance dried at 150°C . gave
 .0712 of BaSO_4 .

	Theory for $\text{C}_{20}\text{H}_{18}\text{BaO}_4$.	Experiment.	
		I.	II.
Carbon	52.28	52.01	—
Hydrogen	3.92	4.15	—
Barium	29.84	—	29.73

III.—*Phenylangelic Acid.*

This acid was discovered by Fittig and Bieber (*Zeitschr. f. Chem.*, 1869, p. 332), they obtained it by heating butyric chloride and benzoic aldehyde in sealed tubes to 120—130° for a long time. It is produced easily by heating butyric anhydride, butyrate of sodium, and benzoic aldehyde to 180° in sealed tubes. The proportions I have used correspond to those for the preparation of phenylcrotonic acid already given. The purification of the crude product from the sealed tube was also conducted in a similar manner. The specimen analysed was twice crystallised from alcohol.

·235 of substance gave

·6455 of CO₂ and

·146 of H₂O.

	Theory for C ₁₁ H ₁₂ O ₂ .	Experiment.
Carbon	75·00	74·89
Hydrogen	6·83	6·90

It is therefore phenylangelic acid—



It melts at 104° to a colourless liquid, and on cooling, crystallises in small needles (Fittig and Bieber give the fusing point as 81°). It is very soluble in alcohol, and is deposited from this solvent in small white needles, but the mother-liquors on standing sometimes give beautiful transparent solid crystals several millimetres in diameter. It dissolves easily in hot petroleum spirit, but only to a small extent when this solvent is cold. It also dissolves slightly in boiling water, from which it is deposited on cooling in white crystals. When boiled with water it is carried over to a small extent with the steam.

In one experiment ten grams of oil of bitter almonds gave eight and a half grams of this acid before crystallisation from alcohol.

If isobutyric anhydride and sodium isobutyrate be heated with benzoic aldehyde, a crystalline acid is produced; it has not yet, however, been much examined.

Silver salt.—On addition of silver nitrate to a solution of the sodium salt of phenylangelic acid, a white precipitate is formed slightly soluble in cold water.

Chloride of Phenylangelyl, C₁₁H₁₁O.Cl.—A mixture of phenylangelic acid and phosphorus pentachloride, in the proportions of one molecule of each, was gently warmed: chemical action set in energetically, with evolution of hydrochloric acid, and the mixture became fluid. The product was heated in an oil-bath to 140°, and dry air passed through it to remove the phosphorous oxychloride. The resulting product was a pale yellow oil. With water it gradually decomposes, forming a

crystalline mass of phenylangelic acid, and with alcohol it produces an oily ether. Its composition was determined by converting it into the amide.

Phenylangelamide, $C_{11}H_{13}(NH_2)$. — The preceding chloride when shaken with strong aqueous ammonia, yields a yellowish-white solid product which, when washed, dried, and dissolved in boiling alcohol, separates out on cooling in very beautiful prismatic crystals. It gave the following numbers on analysis :—

- I. 2795 of substance gave
 7685 of CO_2 and
 2005 of H_2O .
 II. 2516 of substance gave
 6945 of CO_2 and
 168 of H_2O .

Theory for $C_{11}H_{11}O(NH_2)$.		Experiment.	
		I.	II.
Carbon	75.45	74.98	75.28
Hydrogen	7.42	7.97	7.42

No. II was first crystallised from alcohol, and then from petroleum spirit.

Phenylangelamide is easily soluble in alcohol, but rather difficultly so in petroleum spirit. Boiling water dissolves it to a small extent, from which it crystallises on cooling. It melts at 128° .

Products of the Action of Succinic Anhydride and Sodium Succinate on Benzoic Aldehyde.

Having obtained the results already described, by acting upon benzoic aldehyde with the anhydride and the corresponding salt, of monobasic acids it was thought that it would be interesting to make similar experiments, using anhydrides of dibasic acids.

For this purpose succinic anhydride was selected, and heated with sodium succinate and benzoic aldehyde in sealed tubes, to about 180° , for seven or eight hours. The product was a brownish-red sticky substance, and on opening the tubes very large quantities of carbonic anhydride escaped, the product at the same time swelling up to a spongy mass.

The product had no smell of benzoic aldehyde; when boiled with water it fused to a red-brown thick oil, a pale yellow solution being formed. The oily product after repeated boiling with water became, on cooling, a brittle mass, soluble in alkalis.

The aqueous solution on cooling, after standing for some time, deposited nearly colourless crystals, which were in the form of beautiful leafy plates or long needles; these were collected, well washed with

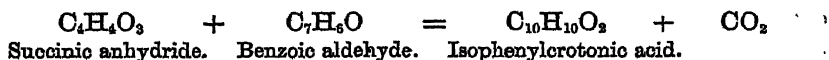
water, and afterwards boiled in water. At first the crystals fused to an oil, but after some time almost entirely dissolved. The solution was filtered and allowed to cool, when it deposited beautiful white needles of the new product. This substance gave the following numbers on analysis:—

- I. .254 of substance gave
 .690 of CO_2 and
 .141 of H_2O .
 II. .256 of substance gave
 .694 of CO_2 and
 .144 of H_2O .

		Experiment.	
The formula $\text{C}_{10}\text{H}_{10}\text{O}_2$ requires		I.	II.
Carbon	74.07	74.08	73.91
Hydrogen	6.17	6.16	6.25

This substance, which is an acid, has therefore the composition of phenylcrotonic acid already described. It is, however, very different in properties; I have therefore named it *isophenylcrotonic acid*.

The formation may be expressed thus, leaving out the succinate, the presence of which is necessary, but its action at present not understood.



Isophenylcrotonic acid melts at about the same temperature as its isomeride obtained from benzoic aldehyde, propionic anhydride, &c., viz., at 83—84°, and when strongly heated it gives off vapours of a suffocating character, somewhat like succinic acid. The fused acid on cooling solidifies to a beautiful crystalline mass. It is excessively soluble in alcohol.

Silver salt, $\text{C}_{10}\text{H}_8\text{AgO}_2$.—A portion of the acid was mixed with sodium carbonate in the proportions of two molecules of acid to one of carbonate. On heating the mixture the acid dissolved with effervescence. Silver nitrate was added to this solution when cold, in small quantities, and the resulting precipitate filtered off. The filtrate was then mixed with an excess of silver nitrate, which caused the formation of an extremely bulky and very curdy precipitate. After standing for some time, with repeated stirring to ensure complete mixing, it contracted somewhat in bulk. It was then collected on a filter, thoroughly washed with cold water and dried. On analysis it gave the following numbers:—

- I. .383 of substance gave
.154 of silver = 40.2 per cent.
- II. .3535 of substance gave
.1415 of silver = 40.02 per cent.

The formula $C_{10}H_8AgO_3$ requires 40.14 per cent. of silver.

It is proposed to continue the investigation of this acid, in order to obtain a more complete account of its history, and to endeavour to produce some of its homologues by the use of other dibasic anhydrides, &c.

Having obtained the foregoing results with benzoic aldehyde, experiments were made in a similar manner with

Cuminic
Cinnamic
Anisic
and Methylsalicylic aldehydes.

The following results were obtained.

ACIDS FROM CUMINIC ALDEHYDE.

I. *Cumenylacrylic or Isopropylphenylacrylic Acid.*

The cuminic aldehyde employed in the following experiments was obtained by simply fractioning oil of cumin, the presence in it of a small quantity of cymene being of no consequence.

A mixture of the aldehyde with dry sodium acetate and acetic anhydride in the proportions of two parts of aldehyde, one part of sodium acetate and three parts of acetic anhydride, was heated in sealed tubes to a temperature of 175° for five or six hours; the resulting product on cooling was a pale brown radiating crystalline mass, and on opening the tubes, carbonic anhydride escaped, but not in very large quantities.

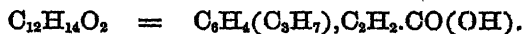
The solid product, when boiled in a retort with water, gave a distillate containing a small quantity of unchanged cuminic aldehyde. When this had ceased to come over, the distillation was stopped. The remaining product in the retort was a brownish oil mixed with an aqueous fluid, the former on cooling solidified to a crystalline mass, and the latter deposited fine white needles. The entire product was thrown on a filter and washed with water. It was then boiled with a solution of sodium carbonate, in which it mostly dissolved, leaving but a small quantity of a neutral brown oil. On filtering the alkaline solution and acidifying it with hydrochloric acid, an acid separated as a nearly white precipitate, which was collected, washed, dried, and

then purified by two or three crystallisations from alcohol. At first the crystals were of a somewhat drab colour, but a few recrystallisations rendered them perfectly white. By this process I have obtained fifty-five per cent. of crystallised acid from the aldehyde employed. It gave the following numbers on analysis:—

I.	·2235 of substance gave
	·618 of CO ₂ and
	·154 of H ₂ O.
II.	·2595 of substance gave
	·720 of CO ₂ and
	·174 of H ₂ O.
III.	·252 of substance gave
	·698 of CO ₂ and
	·168 of H ₂ O.

Theory for C ₁₂ H ₁₄ O ₂		Experiment.		
	I.		II.	III.
Carbon.....	75·78	75·36	75·66	75·55
Hydrogen.....	7·36	·7·65	7·43	7·41

This acid I propose to call *cumenylacrylic acid*—



It crystallises in beautiful pure white needles, which appear to consist of oblique prisms. It is freely soluble in alcohol, and in hot glacial acetic acid, but in boiling water it is only slightly soluble.

At 157—158° it melts, forming a clear fluid, which solidifies to a crystalline mass on cooling. When heated until it boils, carbonic anhydride is given off, a hydrocarbon being formed at the same time.

Cold fuming nitric acid dissolves it, small crystals of a nitro-acid soon separating out from the solution. This, when freed from nitric acid, crystallises from alcohol in yellow needles.

Cumenylacrylic acid is not rapidly acted upon by an aqueous solution of chromic acid, even when boiling; it is, however, gradually decomposed, and an oil distils over, having the odour and properties of cuminic aldehyde.

A solution of this acid in carbon disulphide, when treated with bromine, deposits crystals of a new derivative, which is decomposed when heated with alkalis. This is under examination.

Cinnamic acid, when treated with hypochlorous acid, yields phenylchlorolactic acid. A similar experiment was made with cumenylacrylic acid, but on passing chlorine into its alkaline solution, it became turbid, and oily products containing chlorine separated out.

Ammonium salt.—A solution of cumenylacrylic acid in aqueous ammonia, when evaporated in a vacuum over sulphuric acid, dries up to a mass of silky asbestos-like crystals, which give off ammonia with caustic alkalis. This salt is not easily soluble in water.

Sodium salt.—Obtained by boiling the acid with the theoretical quantity of a solution of sodium carbonate. It quickly dissolves, with evolution of carbonic anhydride, and when evaporated in a vacuum the solution dries up to a white mass, very indistinctly crystalline. It is moderately soluble in water, but precipitated from its solution by sodium chloride; when strongly heated a good deal of a hydrocarbon distils off. Hydrochloric acid precipitates the cumenylacrylic acid from this salt as a beautiful snow-white flocculent powder.

Calcium salt, $C_{24}H_{26}CaO_4$. This is obtained by adding calcium chloride to an aqueous solution of the sodium salt. It comes down as a white crystalline bulky precipitate, which is collected, washed with cold water, and crystallised from boiling water. In this manner it is obtained in small but beautifully white needles. It is difficultly soluble in water; dried in a vacuum it gave the following numbers:—

- I. .297 of substance gave
 .0955 of $CaSO_4 = 9.45$ p.c. calcium.
- II. .416 of substance gave
 .137 of $CaSO_4 = 9.68$ p.c. calcium.

The formula $C_{24}H_{26}CaO_4$ requires 9.58 p.c. of calcium.

This salt when heated to between 90° and 100° in air free from carbonic anhydride, rapidly increases in weight owing to the absorption of oxygen until an amount of that gas has been taken up equal to about one atom. On decomposing this oxidised salt with hydrochloric acid, a white easily decomposable acid is obtained, which is now under investigation. It is believed to be *oxycumenylacrylic acid*, $C_{12}H_{14}O_3$.

Barium salt.—Obtained by double decomposition. It is a white powder, apparently slightly crystalline. Sometimes it conglomerates to a plastic mass when boiled with water, in which it is slightly soluble.

Strontium salt, $C_{24}H_{26}SrO_4 \cdot 2H_2O$.—Similar to the barium salt, being a white powder slightly soluble in water. A specimen dried in a vacuum gave on analysis 17.62 per cent. of strontium; the above formula requires 17.42 per cent.

Copper salt.—This is obtained as a beautiful green precipitate on adding a solution of copper sulphate to the sodium salt.

The *ferric salt* is precipitated as a bulky light brown product on adding iron perchloride to a solution of the sodium salt.

Silver salt, $C_{12}H_{14}AgO_2$.—On adding silver nitrate to a hot solution

of the sodium salt, a copious and bulky precipitate forms; after a short time this contracts, and when viewed under the microscope is seen to be crystalline; when dry it is extremely electric. It gave the following numbers on analysis:—

- I. .368 of substance gave
 .133 of silver = 36.14 per cent.
 II. .258 of substance gave
 .094 of silver = 36.43 per cent.

The above formula requires 36.36 per cent. of silver.

Chloride of Cumenylacryl, $C_{12}H_{13}OCl$.—Cumenylacrylic acid when heated with phosphorus pentachloride (in the calculated proportions) rapidly changes, the mixture becoming fluid, and hydrochloric acid being given off in abundance. On distilling off the oxychloride of phosphorous by heating the product to 130° in an oil-bath, and finally by passing dry air through it at the same temperature, the liquid becomes pale red, and exhibits a blood-red fluorescence. This coloration is undoubtedly due to some slight decomposition, caused by over heating.

When cold, the chloride of cumenylacryl solidifies to a beautifully crystalline mass, fusible at about 25° . On exposure to the air, the moisture soon reconverts it into the acid. On mixing it with alcohol, heat is evolved, and an oil heavier than water is produced; this is undoubtedly the ether.

The formula of this substance was determined by converting it into the amide.

Cumenylacrylamide, $C_{12}H_{13}O(NH_2)$.—Aqueous ammonia acts quickly on the chloride of cumenylacryl, producing a white powder, insoluble, or nearly so, in water. This, when washed and dried, was purified by crystallisation from alcohol, in which it is moderately soluble. In this manner it is obtained in beautiful satiny plates, not unlike flakes of sublimed naphthalene. It gave the following numbers on analysis:—

.272 of substance gave
 .7575 of CO_2 and
 .196 of H_2O .

Theory for $C_{12}H_{13}O(NH_2)$.		Experiment.
Carbon	76.19	75.95
Hydrogen	7.90	8.0

This amide melts at 185 — 186° , and when further heated, distills with apparently but little decomposition, though small quantities of ammonia are given off.

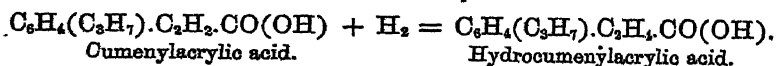
Boiling aqueous potash does not decompose it, unless the solution be a saturated one, when ammonia is freely given off.

Hydrocumenylacrylic or Cumenylpropionic Acid.—To a quantity of cumenylacrylic acid, mixed with about 15 times its weight of water a sufficient amount of sodium amalgam (containing 2 per cent. of sodium) was added, to form its sodium salt. The mixture was frequently agitated. The acid then gradually dissolved, very little hydrogen being given off; excess of sodium amalgam was afterwards introduced, and the mixture left for several hours until hydrogen was pretty freely evolved. After the separation of the amalgam, the solution was acidified with hydrochloric acid, which precipitated the new acid in a crystalline condition. It was collected, washed with water, and pressed between bibulous paper, then dissolved in warm glacial acetic acid, and the solution filtered from a small amount of an amorphous insoluble product. To the clear filtrate water was added by degrees, which caused the new acid to separate in satiny scales, enough water being eventually added to cause nearly the whole of the acid to separate. After standing for several hours, it was collected on a filter, well washed with water, dried in a vacuum, and then fused. On analysis, it gave the following numbers:—

.2627 of substance gave
 .7175 of CO_2 and
 .194 of H_2O .

Theory for $\text{C}_{12}\text{H}_{16}\text{O}_2$.		Experiment.
Carbon	75.0	74.48
Hydrogen	8.3	8.19

The production may be expressed thus:—



Hydrocumenylacrylic Acid fuses at 70° to a clear oil crystallising very beautifully on cooling. It is very soluble in hot alcohol, petroleum-spirit, and glacial acetic acid, but insoluble, or nearly so, in water.

It dissolves in boiling sodium carbonate, forming a clear solution of its sodium salt.

The barium and calcium salts are white precipitates, which when rubbed with a glass rod, become tenacious.

The copper-salt is a bright blue-green precipitate.

Silver salt, $\text{C}_{12}\text{H}_{16}\text{AgO}_2$.—This was prepared by double decomposition with the sodium salt and silver nitrate, rejecting the first portions thrown down. It is a white precipitate, nearly insoluble in water. Dried in a vacuum, and then at 100° , it gave the following numbers on analysis:—

- I. .4025 of substance gave
 .145 of silver = 36.00 per cent.
 II. .3082 of substance gave
 .111 of silver = 36.05 per cent.

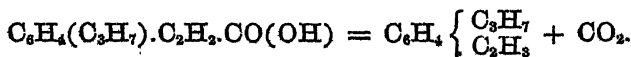
Theory for the above formula requires 36.12 per cent. silver.

Isopropylcinnamene, or Isopropylvinylbenzene.—When cumenylacrylic acid is gently boiled in a bulb-tube with a long neck, into which a side delivery-tube is fixed, the heat being so moderated that a thermometer placed in the upper part of the neck does not indicate more than about 200—210°, a colourless oil distils over, and eventually scarcely anything is left in the bulb-tube. This oil, when washed with aqueous potash, dried over solid potash, and finally distilled from sodium, begins to boil at about 190°, the greater portion coming over between 195—200°. A specimen collected between these temperatures gave the following numbers:—

.2256 of substance gave
 .747 of CO₂ and
 .205 of H₂O.

	Theory for C ₁₁ H ₁₄ .	Experiment.
Carbon.....	90.41	90.3
Hydrogen.....	9.58	10.0

The formation of this substance may be expressed thus:—



Isopropylvinylbenzene has a pleasant fragrant odour. It resinifies when exposed to the air, and seems to be easily changed, forming a tenacious product which probably corresponds with metacinnamene.

II.—*Cumenylcrotonic Acid.*

On heating a mixture of two parts of cuminic aldehyde, one part of sodium acetate, and three parts of propionic anhydride in sealed tubes for about five or six hours to 180°, a viscid product was obtained, which, on cooling, became a pale yellow crystalline mass. This, when boiled with water in a retort to remove unaltered cuminic aldehyde, left with the solution of sodium propionate an oily body, which, on standing, became a crystalline mass. This was collected, washed, dissolved in dilute boiling sodium carbonate, and filtered through a wet filter to separate it from a neutral brownish semi-resinous impurity; the clear solution was then boiled and acidified with hydrochloric acid, which caused the new acid to separate as an oil, solidifying on cooling to a

crystalline mass. This was washed and crystallised from alcohol, from which it separated in crystalline nodular masses. Subsequently, it was found better to use petroleum-spirit as the solvent; from this it crystallises in beautiful oblique prisms. The above process has usually given about 50 per cent. of pure acid from the aldehyde employed. It gave the following numbers on analysis:—

- I. .257 of substance gave
 .723 of CO_2 and
 .179 of H_2O .
 II. .280 of substance gave
 .785 of CO_2 and
 .198 of H_2O .

	Theory for $\text{C}_{13}\text{H}_{16}\text{O}_2$.	Experiment.	
		I.	II.
Carbon.....	76.42	76.72	76.5
Hydrogen	7.84	7.73	7.86

It is, therefore, *cumenylcrotonic acid*,



Cumenylcrotonic acid melts at about $90-91^\circ$. On cooling, it crystallises, and then swells up in a most remarkable manner into leaf-like scales. It is easily soluble in alcohol and in boiling petroleum-spirit, though but little so when the solvent is cold.

Silver salt, $\text{C}_{13}\text{H}_{15}\text{AgO}_2$.—A quantity of cumenylcrotonic acid was dissolved in a solution containing the theoretical weight of sodium carbonate. A few drops of silver nitrate were added, and the resulting precipitate filtered off; excess of silver nitrate was then added to the filtrate, which caused a copious white curdy precipitate to form, rendering the fluid semi-solid, but by stirring and after standing for some time, it became more dense. It was collected on a filter, washed with cold water in which it is nearly insoluble, and dried. It is of a very pure white colour. On analysis, it gave the following numbers:—

- I. .301 of substance gave
 .104 of silver = 34.55 per cent.
 II. .2355 of substance gave
 .0815 of silver = 34.6 per cent.

The above formula requires 34.72 per cent. silver.

III.—*Cumenylangelic Acid*.

A mixture of cuminic aldehyde, butyric anhydride, and sodium butyrate, in proportions corresponding to those used for the previous acids, was heated to 180° for five or six hours in a sealed tube.

The product was a thick pale-brown fluid, and on opening the tube, a little carbonic anhydride was given off. In a second operation, sodium acetate was substituted for butyrate. As in the other experiments, the products were purified by distilling off the unchanged aldehyde with water and dissolving the crude acid in sodium carbonate (having previously washed it with water to remove the saline matter), then precipitating the acid from the filtered solution, and finally crystallising two or three times from alcohol. The resulting product gave the following numbers on analysis:—

- I. .313 of substance gave
 .880 of CO₂ and
 .229 of H₂O.
 II. .258 of substance gave
 .727 of CO₂ and
 .190 of H₂O.

	Theory for C ₁₄ H ₁₈ O ₂ .	Experiment.	
		I.	II.
Carbon	77.06	76.68	76.90
Hydrogen	8.25	8.11	8.18

(Analysis II was made with the product in which sodium acetate was employed.)

This acid is, therefore, *cumenylangelic acid*,



It melts at 123°. Alcohol dissolves it freely, especially when hot, and on cooling deposits it in colourless needles.

ACIDS FROM CINNAMIC ALDEHYDE.

In most of the following experiments pure cinnamic aldehyde was used, prepared from oil of cassia or of cinnamon, by means of a bisulphite. (The pure aldehyde was found to boil at 247—248°.) Oil of cinnamon, however, if of the best quality, answered the purpose very well.

I.—*Cinnamemylacrylic Acid*.

A mixture of two parts of cinnamic aldehyde, three parts acetic anhydride, and one part of sodium acetate, heated to 160—167° in a sealed tube, yields a brown product, which, on cooling becomes a radiated crystalline mass. On opening the tube, carbonic anhydride escapes. On mixing the product with water, the saline matter dissolves and leaves a resinous substance, which, when boiled with sodium carbonate, only partially dissolves. The alkaline solution, after filtration, when acidified with hydrochloric acid, gives a white

precipitate of the new acid, which is purified by crystallisation from alcohol, and then from petroleum-spirit.

A flask, with a condensing-tube, may be used with advantage instead of a sealed tube, in the preparation of this acid, heating it by placing it in a paraffin-bath. The amount of resinous matter produced is always large, and up to the present time I have been unable to obtain more than twenty-five per cent. of this acid from the aldehyde employed. It gave the following numbers on analysis:—

- I. 2565 of substance gave
 - 713 of CO₂ and
 - 141 of H₂O.
- II. 3415 of substance gave
 - 948 of CO₂ and
 - 180 of H₂O.

Theory for C ₁₁ H ₁₀ O ₂ .		Experiment.	
		I.	II.
Carbon	75·85	75·81	75·71
Hydrogen	5·74	6·09	5·83

I propose to call this acid *cinnamenylacrylic*, giving the name cinnamenyl to the radical C₈H₇ = C₆H₅.C₂H₂, which is related to cinnamene in the same manner as cumenyl is to cumene:—



Cinnamenylacrylic acid melts at 165—166°. It is easily soluble in alcohol, from which it crystallises in thin plates. In petroleum-spirit, it is difficultly soluble, but crystallises from it better than from alcohol.

When boiled in a retort with aqueous chromic acid, it gives a distillate containing an oil which appears to be cinnamic aldehyde.

The acid, when heated and boiled, decomposes, yielding an oil which burns with a very smoky flame.

Sodium salt.—Cinnamenylacrylic acid dissolves slowly in a dilute boiling solution of sodium carbonate, and if theoretical quantities are employed, the solution, on evaporation, dries up to a white, almost amorphous mass, not very soluble in cold water.

Calcium salt.—This is obtained by adding calcium chloride to a solution of the sodium salt. It is obtained as a white precipitate, dissolving to a small extent in boiling water, from which it separates in small glistening crystals on cooling.

Barium salt.—Barium chloride gives, with the sodium salt, a white precipitate slightly soluble in water, and separating from the boiling solution on cooling in small needles.

Magnesium salt.—Magnesium sulphate added to a dilute solution of

the sodium salt produces a white milky precipitate, which almost immediately redissolves, but on standing, the salt is deposited in a crystalline state.

Silver salt, $C_{11}H_9AgO_2$.—Obtained by double decomposition as a white, somewhat curdy, precipitate, slightly soluble in water, and blackening gradually in sunlight. It gave the following numbers on analysis:—

- I. 4265 of substance gave
1635 of silver = 38.33 per cent.
- II. 309 of substance gave
119 of silver = 38.51 per cent.

The above formula requires 38.07 per cent. of silver.

Lead salt, a white curdy precipitate.

Copper salt, a pale green precipitate.

Ferric salt, a pale brown precipitate.

Chloride of Cinnamenylacryl, $C_{11}H_9OCl$.—Cinnamenylacrylic acid, when heated gently with phosphorus pentachloride, is rapidly acted upon with evolution of hydrochloric acid, the mixture becoming fluid. On cooling, the chloride separates out in small crystals, rendering the product nearly solid.

Cinnamenylacrylamide, $C_{11}H_9O(NH_2)$.—On agitating the above chloride with strong aqueous ammonia a white product, insoluble in water, is obtained; this, when washed and dried, crystallises from alcohol in flat needles like benzoic acid. It is rather easily soluble in alcohol. On analysis it gave the following numbers:—

2595 of substance gave
725 of CO_2 and
151 of H_2O .

Theory for $C_{11}H_9O(NH_2)$.		Experiment.
Carbon	76.30	76.19
Hydrogen	6.35	6.46

Hydrocinnamenylacrylic acid. On treating cinnamenylacrylic acid with sodium-amalgam by degrees (the acid being suspended in a large excess of water) it dissolved; excess of amalgam was then added, and the mixture allowed to stand about twelve hours. The clear solution was then decanted, acidified with hydrochloric acid, and agitated with ether. The ethereal solution thus obtained left the new acid on evaporation as an oily fluid, which was analysed and gave the following numbers:—

2695 of substance gave
7365 of CO_2 and
162 of H_2O .

Theory for $C_{11}H_{12}O_2$.		Experiment.
Carbon	75.0	74.52
Hydrogen	6.81	6.68

Silver salt, $C_{11}H_{11}AgO_2$.—This is a white precipitate, and gave the following numbers on analysis:—

- 400 of substance gave
- 1505 of silver = 37.62 per cent.

The above formula requires 38.16 per cent. of silver.

The analytical results obtained with this acid are not so satisfactory as could be desired, but I had but little product at my disposal. The numbers, however, indicate that only two atoms of hydrogen united with the cinnamethylacrylic acid, and not four, as was thought probable.

If the formula given be correct, this acid is isomeric with phenylangelic acid.

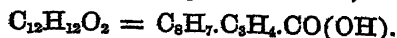
II. *Cinnamethylcrotonic Acid.*

In the preparation of this acid the proportions used were six grams of sodium propionate, fifteen grams of cinnamic aldehyde, and fifteen grams of propionic anhydride. The mixture was heated in a sealed tube to 160—165° C. for about six hours. On opening the tube only a small quantity of carbonic anhydride escaped. The product was boiled with water to remove volatile products, and allowed to cool, then thrown on a filter to separate sodium propionate, boiled with sodium carbonate, and the resulting solution filtered. The new acid was then precipitated with hydrochloric acid, washed, crystallised once from alcohol, and finally twice from petroleum spirit. The above quantities yielded five grams of acid. It gave the following numbers on analysis:—

- 2710 of substance gave
- 7585 of CO_2 and
- 158 of H_2O .

Theory for $C_{12}H_{12}O_2$.		Experiment.
Carbon	76.59	76.31
Hydrogen	6.39	6.48

This acid is therefore *cinnamethylcrotonic acid*,—



It melts at 157—158°. It is nearly insoluble in cold, and difficultly in hot petroleum spirit. From this solvent it crystallises in flat, oblique, transparent prisms, which become opaque on keeping. It is easily soluble in alcohol.

Sodium salt.—The above acid dissolves slowly in a boiling dilute solution of sodium carbonate. On evaporating it in a vacuum it forms a distinctly crystalline product only moderately soluble in water.

Calcium salt.—This separates from the sodium salt on the addition of calcium chloride, as a flocculent white precipitate, which dissolves if boiled in a very large excess of water, and crystallises out on cooling in groups of minute needles.

Barium salt.—Obtained by double decomposition, is a flocculent precipitate, difficultly soluble in boiling water. It is deposited from its aqueous solution on cooling in minute crystals, which, when seen with a lens, appear like crystals of benzoic acid.

The *magnesium salt* is a crystalline body more easily soluble than the two preceding.

The *ferric salt* is a pale drabish-brown precipitate.

The *copper salt* is a very pale green precipitate.

Silver salt, $C_{12}H_{11}AgO_2$.—This is of a pure white colour, slightly soluble in cold water, and but slowly acted upon by light. It gave the following numbers on analysis:—

I. .410 of substance gave
 .149 of silver = 36.34 per cent.

II. .4055 of substance gave
 .1475 of silver = 36.37 per cent.

The above formula requires 36.6 per cent. silver.

III. *Cinnamemylangelic Acid.*

The products used in the preparation of this acid were employed in the proportion of one of sodium butyrate, two of cinnamic aldehyde, and three of butyric anhydride, and the sealed tubes were heated to 160—165° for about six hours. The resulting substance was boiled with water until oily products ceased to distil over. The residue in the retort was allowed to cool, and the crude acid collected on a filter and washed with water, boiled with sodium carbonate, the solution filtered, and the acid precipitated with hydrochloric acid. It was then dried and crystallised from petroleum spirit. On analysis, however, it did not give satisfactory numbers. It was then further purified by conversion into the calcium salt, which was boiled with water, thrown on a filter, and washed with hot water. The salt was then decomposed with hydrochloric acid, the product washed, dried, and crystallised from petroleum spirit. There was first formed a bulky mass of minute crystals almost filling the liquid; in a few hours, however, they changed, becoming brilliant and occupying a small space. They were very beautiful when viewed under the microscope.

The following numbers were obtained on analysis :—

- I. .254 of substance gave
 .7177 of CO_2 and
 .1544 of H_2O .
 II. .2388 of substance gave
 .673 of CO_2 and
 .146 of H_2O .

Theory for $\text{C}_{13}\text{H}_{14}\text{O}_2$		Experiment.	
		I.	II.
Carbon	77.22	77.04	76.84
Hydrogen	6.93	6.75	6.79

It is, therefore, *cinnamemylangelic acid*,—



This acid melts at $125\text{--}127^\circ$. It is easily soluble in alcohol, but not very freely so in petroleum spirit.

Silver salt, $\text{C}_{13}\text{H}_{13}\text{AgO}_2$.—On adding a small quantity of silver nitrate to a solution of the sodium salt of this acid, a precipitate forms, but redissolves in the excess of the sodium salt. On adding a large quantity, however, a white precipitate is obtained, slightly soluble in cold water. It gave the following numbers on analysis :—

- I. .315 of substance gave
 .1105 of silver = 35.08 per cent.
 II. .218 of substance gave
 .0765 of silver = 35.05 per cent.

The above formula requires 34.95 per cent. silver.

ACIDS FROM ANISIC ALDEHYDE.

I. *Methylparoxyphenylacrylic Acid*.

A mixture of two parts of anisic aldehyde, two of acetic anhydride, and one of sodium acetate, heated to about 170° in sealed tubes for eight hours, gave a dark-coloured product, and on opening the tubes carbonic anhydride escaped. The contents of the tubes were boiled with water in a retort until the distillate was nearly free from oil, the residue was then allowed to cool, and the crystalline product collected on a filter and washed from saline matter. It was then boiled with sodium carbonate, filtered through a wet filter to remove neutral oily products, and the new acid precipitated with hydrochloric acid. After being washed and dried, it was twice crystallised from alcohol. It gave on analysis the following numbers :—

- I. .283 of substance gave
 .696 of CO₂ and
 .145 of H₂O.
 II. .205 of substance gave
 .5065 of CO₂ and
 .105 of H₂O.

Theory for C ₁₀ H ₁₀ O ₃ .		Experiment.	
		I.	II.
Carbon	67.41	67.07	67.33
Hydrogen	5.61	5.69	5.66

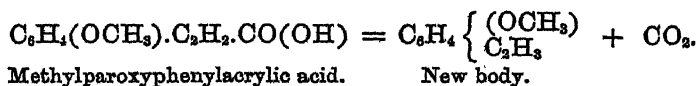
It is, therefore, *methylparoxyphenylacrylic acid*,—



and, therefore, the methylic derivative of paracoumaric acid, which is paroxyphenylacrylic acid.

Methylparoxyphenylacrylic acid melts at about 171°. It is moderately soluble in alcohol, from which it crystallises in very pale yellow needles. It also dissolves rather freely in hot glacial acetic acid. In boiling water it is soluble, but only to a small extent, this solution on cooling deposits the acid in small white crystals.

On heating till it boils, decomposition takes place, an oil having a strong but pleasant odour of fennel being produced; when cooled it solidifies to a crystalline mass. It is most probably a homologue of anethol, and produced thus:—



Methylparoxyphenylacrylic acid, when boiled in a retort with dilute chromic acid, is slowly oxidised, and an oil distils over, which is apparently anisic aldehyde.

Sodium salt, C₁₀H₉NaO₃.—This is obtained by boiling a weighed quantity of the acid with the theoretical quantity of a standard solution of sodium carbonate. It is deposited on cooling as a white mass, appearing under the microscope to consist of minute crystals with a satiny lustre. It is rather difficultly soluble in water. An analysis of the crystals dried in a vacuum gave the following result:—

- .328 of substance gave
 .117 of sodium sulphate = 11.67 p.c.

The above formula requires 11.50 p.c. of sodium.

Calcium salt.—Obtained in the form of transparent needles on

adding calcium chloride to a weak boiling solution of the sodium salt, filtering, and leaving the mixture to cool.

Barium salt.—Prepared in an analogous manner to the calcium salt, is obtained as a crystalline precipitate.

Strontium salt.—Deposited from its boiling aqueous solution on cooling in small crystals, more soluble than the barium salt.

Copper salt.—Obtained by double decomposition. It is a pale bluish-green precipitate.

Ferric salt.—A brown precipitate.

Silver salt, $C_{10}H_4AgO_3$.—A dilute solution of the sodium salt was treated with silver nitrate until a small quantity of a precipitate was produced, and not redissolved on stirring; the solution was then filtered, and silver nitrate added in excess. The pure white precipitate then produced was collected, washed and dried in a vacuum. It gave on analysis the following numbers:—

- I. .3137 of substance gave
 .1185 of silver.
- II. .3815 of substance gave
 .588 of CO_2 and
 .1118 of H_2O and
 .144 of silver.

Theory for $C_{10}H_4AgO_3$.		Experiment.	
		I.	II.
Carbon	42.10	—	42.03
Hydrogen	3.16	—	3.23
Silver	37.89	37.77	37.74

This salt is slightly soluble in water.

Chloride of Methylparoxyphenylacryl.—When methylparoxyphenylacrylic acid and phosphorous pentachloride are heated together in a flask by means of a water-bath, chemical action quickly sets in, hydrochloric acid is evolved, and the mixture becomes fluid. After removing the phosphorous oxychloride by heating the product in an oil-bath to $120-130^\circ$, and then passing dry air, the new product is left as a somewhat dark yellowish oil, which on cooling solidifies to a beautifully crystalline mass, fusing at about 50° .

When mixed with alcohol it reacts with evolution of heat, and produces the ether, which is a pale yellow viscid oil heavier than water.

Methylparoxyphenylacrylamide, $C_{10}H_8O_2(NH_2)$.—The chloride just described when mixed with alcoholic ammonia becomes hot, and deposits crystals. On evaporating off the alcohol and treating the residue with water, a white product is left. This was purified by crystallisation from water, and gave the following numbers on analysis:—

- I. .2619 of substance gave
 .648 of CO₂ and,
 .156 of H₂O.
 II. .3265 of substance gave
 .808 of CO₂ and
 .178 of H₂O.

Theory for C ₁₀ H ₉ O ₂ (NH ₂).		Experiment.	
		I.	II.
Carbon	67.79	67.46	67.47
Hydrogen	6.21	6.6	6.1

This amide melts at 186°, and crystallises on cooling. It is deposited in scaly crystals from alcohol, in which it is very soluble. It is not easily soluble in water, and the crystals obtained from this solvent are very small.

Hydromethylparoxyphenylacrylic Acid or Methylparoxyphenylpropionic Acid.

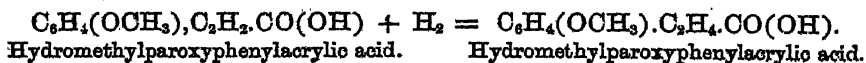
One part of methylparoxyphenylacrylic acid was mixed with fifty parts of water, and sodium amalgam containing two per cent. of sodium, added by degrees, the mixture being constantly agitated. When the acid had dissolved, excess of amalgam was added, and the mixture allowed to stand twenty-four hours. The clear solution was then separated from the mercury and acidified with hydrochloric acid. A copious white crystalline precipitate separated, which after standing for several hours, was thrown on a filter, and washed with cold water. It was then purified, by solution in boiling water, and filtering from a small amount of insoluble impurity. On cooling, the new acid was deposited in feathery crystals.

This product gave on analysis the following numbers:—

- .2746 of substance gave
 .669 of CO₂ and
 .166 of H₂O.

Theory for C ₁₀ H ₁₁ O ₃ .		Experiment.	
Carbon	66.66	66.44	
Hydrogen	6.66	6.73	

This acid melts at 101°. Its formation may be expressed thus—



II. *Methylparoxyphenylcrotonic Acid.*

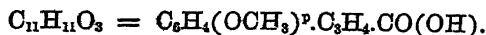
Two parts of anisic aldehyde, three parts of propionic anhydride, and one part of sodium propionate were the proportions used in the prepara-

tion of this acid. The mixture was heated in sealed tubes to about 170—175° for six hours. The product when boiled with water to remove unconverted anisic aldehyde, was left as an oily layer, solidifying on cooling to a crystalline cake. The aqueous solution containing the sodium propionate also deposited the new acid in beautiful thin plates. The crude product after being washed with water was boiled with sodium carbonate, which dissolved most of it, but left a good deal of neutral oily matter. The solution was filtered, but as it was milky, it was found necessary to treat it with ether; it was then boiled and acidified with hydrochloric acid, which caused the new acid to separate as a white precipitate. It was collected, washed, and crystallised from alcohol. On analysis it gave the following numbers:—

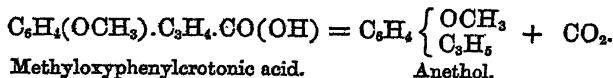
·2865 of substance gave
·719 of CO₂ and
·161 of H₂O.

Theory for C ₁₁ H ₁₂ O ₃ .		Experiment.
Carbon	68·74	68·46
Hydrogen	6·24	6·25

This acid is therefore *methylparoxyphenylcrotonic*,



It melts at 154°. When heated to boiling, it decomposes, yielding an oil which has the odour of oil of anise, and when cooled becomes crystalline. There can be scarcely any doubt that it is anethol; it is under examination. The decomposition may be expressed thus:



Methoxyphenylcrotonic acid is moderately soluble in alcohol, and crystallises from it in beautiful transparent rectangular plates.

Calcium salt.—On adding calcium chloride to a dilute solution of the sodium salt, a crystalline precipitate forms, which dissolves on boiling, and is deposited on cooling in small white needles.

Barium salt.—Prepared in an analogous manner to the calcium salt. It crystallises from its boiling aqueous solution in thin brilliant plates.

Silver salt, C₁₁H₁₁AgO₃.—This is prepared by adding silver nitrate to the sodium salt, filtering off the first portions of the precipitate and then adding an excess of silver nitrate. The salt which comes down as a satiny crystalline precipitate, is slightly soluble in cold water, but

more so in hot water; from the latter it crystallises on cooling in fine needles; it is only slowly acted upon by light. It gave the following numbers on analysis:—

- I. .3800 of substance gave
 .138 of silver = 36.32 p.c.
 II. .3775 of substance gave
 .136 of silver = 36.02 p.c.

The above formula requires 36.12 per cent. of silver.

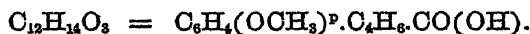
III. *Methylparoxyphenylangelic Acid.*

A mixture of sodium butyrate, anisic aldehyde, and butyric anhydride in the proportions corresponding with those employed in the preparation of the preceding acid, was heated in sealed tubes to 180° for six hours; the product was boiled with water as in the previous cases, and the crude acid, after washing, dissolved in an alkaline carbonate, and filtered from oily impurities. The boiling alkaline solution, when acidified, deposited the new acid as a white precipitate, part of which fused in the hot fluid. It was then crystallised from alcohol four times. In one experiment sodium acetate was used in place of sodium butyrate; the product, however, was not considered to be quite so good, as there appeared to be minute crystals of another acid present; these, however, disappeared on repeated crystallisation. Analysis I. was made with this preparation.

- I. .2832 of substance gave
 .721 of CO₂ and
 .168 of H₂O.
 II. .3165 of substance gave
 .807 of CO₂ and
 .188 of H₂O.

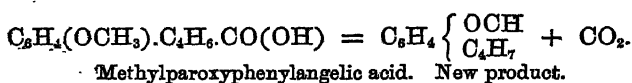
	Theory for C ₁₂ H ₁₄ O ₃ .	Experiment.	
		I.	II.
Carbon.....	69.9	69.43	69.54
Hydrogen	6.79	6.58	6.61

This is therefore *methylparoxyphenylangelic acid*—



It melts at 123—124° to a colourless oil, and on cooling crystallises in a most beautiful manner. It crystallises from alcohol in needles.

If heated until it boils, it decomposes and gives an oil similar in odour to the oil of anise. It is probably another homologue of anethol, and formed thus:



ACIDS FROM METHYLSALICYLIC ALDEHYDE.

I. β^* .—*Methylorthoxyphenylacrylic Acid*.

Two parts of hydride of methyl salicyl, three of acetic anhydride, and one of sodium acetate, were heated in sealed tubes to about 180° for six hours. The contents of the tubes on cooling consisted of two distinct products, one forming small groups of crystals as fine as pin-heads, the rest being a radiating crystalline mass. On opening the tubes, carbonic anhydride escaped. The solid product was boiled with water in a retort as usual, and the crude acid remaining collected on a filter, washed with water, dissolved in boiling sodium carbonate, and then filtered through a wet filter, the clear solution, on being acidified with hydrochloric acid, deposited the new acid as a nearly white precipitate. It was collected, washed, and finally purified by crystallisation from alcohol. It gave, on analysis, the following numbers:—

- I. 283 of substance gave
 7005 of CO_2 and
 141 of H_2O .
 II. 2935 of substance gave
 723 of CO_2 and
 150 of H_2O .

	Theory for $\text{C}_{10}\text{H}_{10}\text{O}_3$.	Experiment.	
		I.	II.
Carbon	67.41	67.50	67.16
Hydrogen	5.61	5.57	5.66

This acid is, therefore, *methylorthoxyphenylacrylic* or *methylcoumaric acid*—



It melts at 182 — 183° . When heated until it boils, it decomposes, yielding an oil, having an odour very unlike that obtained from the *para*-acid, but somewhat similar to that of coal-tar naphtha.

It is moderately soluble in alcohol, and crystallises from it in small hard prisms.

When fused with potassium hydrate, it first becomes yellow, apparently owing to the formation of coumaric acid, but when further heated, it yields salicylic acid in abundance.

When heated with phosphorus pentachloride it decomposes, yielding a chloride. This, when treated with ammonia, is converted into

* The reason why this acid is called β -acid will be seen further on in this paper.

methylorthoxyphenylacrylamide, crystallising from alcohol in needles. It fuses at 191—192°.

Calcium salt is obtained as a white precipitate, becoming crystalline on adding calcium chloride to a solution of the sodium salt.

Barium salt: similar to the above.

Copper salt: a green precipitate.

Ferric salt: a pale brown precipitate.

Silver salt, $C_{10}H_9AgO_3$.—Obtained by adding silver nitrate to a solution of the sodium salt. It is a white precipitate, and gave, on analysis, the following numbers:—

- I. .301 of substance gave
 .1135 of silver = 37.7 per cent.
- II. .3145 of substance gave
 .118 of silver = 37.52 per cent.

The above formula requires 37.8 per cent. of silver.

II.—*Methylorthoxyphenylcrotonic Acid.*

Seventeen grams of hydride of methylsalicyl, twenty-four grams of propionic anhydride, and twelve grams of sodium propionate, were heated in sealed tubes to 165° for five or six hours. The product, on cooling, was a pale-brown crystalline mass. On boiling it with water, some unchanged hydride of methylsalicyl volatilised with the steam, leaving in the retort an oily product, which on cooling, gradually solidified. It was washed from saline matter, and then boiled with sodium carbonate. The solution was filtered from a small quantity of neutral oil, boiled, and acidified with hydrochloric acid. The new acid separated as an oil, but on cooling solidified to a crystalline cake. When cold, it was washed, dried, and crystallised from petroleum spirit. This operation yielded thirteen grams of crude acid before crystallisation. It gave the following numbers on analysis:—

- I. .281 of substance gave
 .705 of CO_2 and
 .157 of H_2O .
- II. .2565 of substance gave
 .646 of CO_2 and
 .1445 of H_2O .

Theory for $C_{11}H_{12}O_3$.		Experiment.	
		I.	II.
Carbon	68.74	68.42	68.68
Hydrogen	6.25	6.20	6.26

This substance is, therefore, *methylorthoxyphenylcrotonic acid*,



It melts at 104–105°. It is very soluble in alcohol and benzol, not very much so in petroleum spirit, but from a boiling solution in this solvent it is deposited on cooling in large leafy crystals arranged in fern-like groups. When heated in a watch-glass, it fuses to a clear oil, and on cooling, crystallises, forming small circular discs, radiating from the centre, and as these increase, they crack with such force as to cause the watch-glass to emit a distinct sound each time. The crystalline mass often shows colours somewhat like those of mother-of-pearl.

Calcium salt.—This comes down as a white crystalline precipitate if calcium chloride be added to a solution of the sodium salt. If the solution be very dilute, it crystallises in beautiful groups of satiny needles; it is more soluble in hot than cold water.

Barium salt, $C_{22}H_{22}BaO_6$.—On adding barium chloride to a boiling solution of the sodium salt somewhat dilute, this compound on cooling, separates out in needles. It is rather soluble in cold water. The crystals appear to contain water of crystallisation, as they change in appearance on drying over sulphuric acid. A specimen dried at 100° gave the following numbers :—

·134 of substance gave

·060 of $BaSO_4$ = 26·32 per cent. of barium.

The above formula requires 26·39 „ „

Silver salt, $C_{11}H_{11}AgO_3$.—Silver nitrate, added in small quantities to a solution of the sodium salt, gives a white precipitate, which, on stirring, dissolves almost entirely; but excess gives a pure white precipitate, which, during washing, contracts to a small bulk, and apparently becomes crystalline. It is slightly soluble in water. On analysis, the following number was obtained :—

·239 of substance gave

·08625 of silver = 36·08 per cent.

The above formula requires 36·02 per cent. silver.

III.—*Methylorthoxyphenylangelic Acid.*

A mixture of one part of sodium butyrate, three of butyric anhydride, and two of hydride of methyl salicyl, was heated in sealed tubes to 165° for about seven hours. The resulting product was a viscid liquid, and on opening the tubes, a good deal of carbonic anhydride escaped. After boiling with water as usual, the residue in the retort contained an oil which on standing for some hours partially solidified. It was separated from the aqueous solution of sodium butyrate, and boiled with a solution of sodium carbonate, which dissolved the new acid, but left a considerable quantity of neutral oil, which was removed from it by means of ether.

The alkaline solution was boiled and acidified with hydrochloric acid: the acid then separated as an oil, but solidified on cooling. It was collected, washed, and again dissolved in sodium carbonate, using about the calculated quantity necessary to form the sodium salt, and converted into the calcium salt by the addition of calcium chloride. This salt came down in a plastic state, adhering to the sides of the vessel, but on cooling, the liquid was filled with small crystals, which appeared as fine needles.

The calcium salt was collected and washed several times with cold water, and then decomposed with hydrochloric acid. The acid thus obtained was twice crystallised from alcohol, from which it separated in hard needles, about three-quarters of an inch in length. It gave the following numbers on analysis:—

·255 of substance gave
·6515 of CO₂ and
·157 of H₂O.

Theory for C ₁₂ H ₁₄ O ₃ .	Experiment.	
	I.	II.
Carbon	69·90	69·67
Hydrogen	6·79	6·83

This is therefore *methylorthoxyphenylangelic acid*—



It fuses at about 105°, is very soluble in alcohol, but much less so in petroleum spirit.

Acids obtained from Coumarin.

As all the aromatic aldehydes experimented on, with the exception of the hydride of salicyl, yield an acid when treated with acetic anhydride and an acetate, there could be no doubt that the formation of coumarin is preceded by that of an acid. This acid would, of course, be an ortho-oxy-compound, and would, therefore, readily split up into water and an anhydride, which would be coumarin. This agrees with the views of the constitution of that substance proposed by Fittig (*Chem. News*, xix, 73).

But coumarin, when treated with potassium hydrate, yields two compounds of the same composition. The first, which was examined by R. Williamson (*Journ. Chem. Soc.*, xxviii, 852), is obtained by simply boiling coumarin with an aqueous solution of the alkali; the second is produced in the same manner, but employing a higher temperature.

The first compound, when decomposed with an acid, yields coumarin; the second, ordinary coumaric acid.

Now it appeared doubtful which of these two alkaline compounds represented the acid of which coumarin is the anhydride, because it was possible that this acid might be so unstable as to split up into coumarin and water as soon as it was liberated; and, on the other hand, that coumaric acid, on account of the high temperature at which it is produced, might be an alteration-product, and not the true acid.

R. Williamson's metallic derivatives must have the constitution $C_6H_4(OR) \cdot C_2H_2.CO(OR)$, which is the same as that of a coumarate, unless they be regarded as molecular compounds, which I think is untenable.

If this constitution be correct, it is evident that these substances, by treatment with methylic iodide, might be expected to yield the compound, $C_6H_4(OMe) \cdot C_2H_2.CO(OMe)$.

This should be the methylic derivative of an acid already described in this paper, namely, methylorthoxyphenyl acrylic, and by treatment with potassium hydrate should be decomposed into its potassium-salt.

Experiments were made in this direction with the following results:—

A quantity of an alcoholic solution of the compound obtained by boiling coumarin with sodium hydrate was treated with iodide of methyl in a sealed tube and heated to 100° for about three hours. On opening the tube, the reaction was found to be complete. The alcohol was distilled off and water added: this caused an oil to separate in quantity.

On distilling this oil it was found to boil at $278-280^\circ$, very little coming over on either side of this temperature. It was analysed, and gave the following numbers:—

I.	·2588 of substance gave
	·6495 of CO_2 and
	·142 of H_2O .
II.	·273 of substance gave
	·6882 of CO_2 and
	·1565 of H_2O .

Theory for $C_{11}H_{12}O_3$.		Experiment.	
		I.	II.
Carbon	68·75	68·44	68·71
Hydrogen	6·25	6·09	6·37

This substance has therefore the composition of the methylic derivative of methylorthoxyphenylacrylic acid, and may be written thus, $C_6H_4(OCH_3) \cdot C_2H_2.CO(OCH_3)$, and is formed from the sodium compound simply by the substitution of that metal by methyl. It is the

methylic ether of an acid I propose to call *α-methylorthoxyphenylacrylic acid*.

A portion of this ether, before it had been distilled, was boiled with alcoholic potassium hydrate, which decomposed it, and after adding water and boiling off the alcohol, hydrochloric acid was added in excess; this caused an oily substance to separate, which crystallised very beautifully on cooling.

This acid was also prepared in a different manner. A quantity of the compound obtained by boiling coumarin with sodium hydrate was dissolved in alcohol and mixed with only enough methylic iodide to combine with *half* the sodium: the mixture was heated in a sealed tube to 150° for five or six hours: the resulting product was a pale-coloured fluid. The alcohol was distilled off, and on cooling a syrupy mass was obtained, and on dissolving it in water only a trace of oily product was found to be present; this was removed with ether. The clear aqueous solution was boiled and acidified with hydrochloric acid; the new acid then separated as an oil, but solidified to a crystalline mass on cooling.

It was not found practicable to purify it by crystallisation from alcohol, but after trying various solvents, ordinary acetic acid (about 50 p.c.) was found to answer the purpose. After crystallisation from this acid, it gave on analysis the following numbers:—

·2458 of substance gave

·608 of CO₂ and

·1245 of H₂O.

Theory for C₁₀H₁₀O₂.

Experiment.

Carbon 67·41 67·45

Hydrogen 5·61 5·62

This compound then has exactly the composition of methylorthoxyphenylacrylic acid, and when fused with potassium hydrate also yields salicylic acid, but in other respects it is entirely different. It melts at 88—89°, the other at 182—183°, and is very much more soluble in alcohol, &c. This is why I have called it *α-methylorthoxyphenylacrylic acid*.

This new acid is moderately soluble in ordinary acetic acid, and separates from it, on cooling, in beautiful glistening crystals, which generally lose their lustre on drying.

Sodium salt.—Obtained by boiling this acid with the theoretical quantity of sodium carbonate. It is excessively soluble in water, and dries up to a gummy mass.

Copper salt: bright yellowish-green precipitate.

Ferrio salt: pale brown precipitate.

Silver salt, C₁₀H₉AgO₃.—This comes down as a white crystalline precipitate on adding silver nitrate to the sodium salt. The filtrate from

this deposits a small quantity of salt, on standing, as a white powder, which when seen under the microscope is composed of distinct crystals. It gave on analysis the following numbers:—

- I. 4118 of substance gave
1558 of silver = 37·83 p.c.
- II. 5102 of substance gave
1927 of silver = 37·76 p.c.

The above formula requires 37·8 p.c.

Action of Heat on some of the above Coumarin Derivatives.

These substances are modified in a remarkable manner when heated. If a mixture of an alcoholic solution of the compound obtained by boiling coumarin with sodium hydrate be mixed with methylic iodide in about theoretical quantities, and heated in a sealed tube to 150°, instead of 100°, the product after removal of the alcohol, &c., is an oil as in the other case; but when decomposed with alcoholic potassium hydrate, yields the salt of an acid which fuses only at a high temperature.

Moreover if the oil produced by heating the sealed tubes to only 100° C. (and which produces a very fusible acid, α -methylorthoxyphenylacrylic acid), be heated alone in a sealed tube to 150—165° for a few hours, and then decomposed with alcoholic potassium hydrate, it yields the same difficultly fusible acid. On examining the oil which was purified by distillation and used for analysis (p. 418), it was found to give on decomposition a mixture of the fusible and difficultly fusible acids; therefore by the influence of heat alone this substance is changed.

This difficultly fusible acid was purified by crystallisation from alcohol and submitted to analysis.

- I. 261 of substance gave
6465 of CO₂ and
132 of H₂O.
- II. 205 of substance gave
506 of CO₂ and
105 of H₂O.

	Theory for C ₁₀ H ₁₀ O ₃	Experiment.	
		I.	II.
Carbon	67·41	67·54	67·31
Hydrogen	5·61	5·61	5·68

It has therefore the same composition as the easily fusible one, but its melting point is 182—183°. It is in fact identical with the acid obtained by treating the hydride of methylsalicyl with acetic anhydride and sodium acetate, and called in this paper β -methylorthoxyphenylacrylic or methylcoumaric acid.

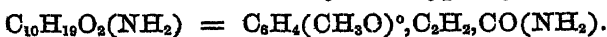
The easily fusible or α -acid on being heated to its boiling-point, and then purified by crystallisation, was found to be changed, and converted into the β -acid fusing at 183° .

It has been seen that the methylic derivative of the α -acid is converted by heat into that of the β -acid. Neither of these compounds are acted upon by alcoholic ammonia at 100° , and of course if the temperature be raised above 150° , the reaction virtually takes place on the β -compounds. On heating a mixture of either of these substances to 200° for 10 or 14 hours, with alcoholic ammonia, the product on cooling deposits crystals: these were collected, recrystallised, and submitted to analysis. The following results were obtained:

- I. .282 of substance gave
 .697 of CO_2 and
 .159 of H_2O .
 II. .2745 of substance gave
 .6795 of CO_2 and
 .157 of H_2O .

	Theory for $\text{C}_{10}\text{H}_9\text{O}_2(\text{NH}_2)$.	Experiment.	
		I.	II.
Carbon	67.79	67.41	67.5
Hydrogen	6.21	6.25	6.35

This substance is therefore β -methylorthoxyphenylacrylamide.



It is moderately soluble in alcohol, from which it crystallises in beautiful white needles. It melts at 191 — 192° .

Action of Pentachloride of Phosphorus on α -Methylorthoxyphenylacrylic Acid.

When this acid is mixed with phosphorus pentachloride, chemical action sets in with energy, and the mixture becomes fluid, hydrochloric acid being abundantly given off. The product, when treated with ammonia, yields an amide insoluble in water. This, when crystallised from alcohol, was found to be β -methylorthoxyphenylacrylamide. The aqueous filtrate from the preparation of this amide on being acidified with hydrochloric acid gave a white precipitate of an acid, which was purified by crystallisation from alcohol. It gave the following numbers:—

- .2415 of substance gave
 .594 of CO_2 and
 .121 of H_2O .

	Theory for $\text{C}_{10}\text{H}_9\text{O}_2$.	Experiment.	
Carbon	67.44	67.08	
Hydrogen	5.61	5.56	

This acid fuses at about 183° , and is therefore β -methylorthoxyphenylacrylic acid.

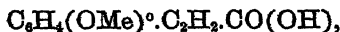
An analogous experiment was made in which carbon disulphide was mixed with the phosphorus pentachloride and the acid, to keep the temperature low, but the result was the same.

We therefore see that heat and also powerful chemical action convert the α - into the β -compounds.

But why are these substances isomeric and not identical? Of course it is evident that two acids having their composition might exist thus :



which is orthoxyphenylacrylate of methyl, or in other words, a coumarate of methyl, and



methylorthoxyphenylacrylic acid, or methylcoumaric acid.

Both of these compounds would form metallic derivatives, and at first sight this might be thought to be an explanation of the difficulty, but I think it is not consistent with experiment.

As already stated, if the methylic ether of the α -acid which is produced at low temperatures, and of course yields the α -acid when treated with alcoholic potassium hydrate, &c., be heated to 150° , it is changed into the β -methylic ether and yields the β -acid.

The methylic ether of the α -acid has all the hydrogens of its hydroxyls replaced by methyl, so that the effect of heat cannot cause any change of position to take place in this respect, and there is no ground for supposing that the alkali in one case should remove the methyl from the phenolic position, and in the other from the $\text{CO}(\text{OH})$ group, experiment always showing that the phenolic is the more difficult to influence of the two.

Again, when the alkaline compound of coumarin obtained by boiling coumarin with caustic alkali is treated with enough methylic iodide to remove half the metal, a salt of the α -acid is produced. In mixed compounds, I believe that the metal replacing phenolic hydrogen, is much more readily acted upon, than that replacing hydrogen in the $\text{CO}(\text{OH})$ group.

If the α -acid were the methyl ether of orthoxyphenylacrylic acid,



we should expect it to give with phosphorus pentachloride methylic chloride and the chloride of orthoxyphenylacryl; in fact, to behave like oil of gaultheria under similar circumstances; but instead of this,

it is converted into the chloride of the β -acid, yielding, with ammonia, the amide.

These acids being both derived from coumarin, which is an ortho-compound, are necessarily ortho-acids, which is also seen by their yielding salicylic acid when fused with potassium hydrate; and if coumarin be the anhydride of coumaric acid, it is difficult to understand that there can be any difference of structure in the group which represents the radicle of these acids, viz. :—



so that it appears probable that we must seek for an explanation of their isomerism from other sources than that of position.

From the formation of the α -acid there can be no doubt that the metallic compounds of coumarin examined by R. Williamson are salts of an unstable acid, isomeric with coumaric acid.

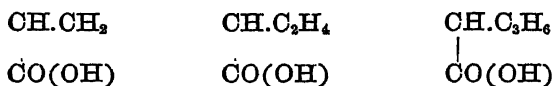
I hope to investigate this subject more fully, and to make analogous experiments with the homologues of coumarin.

Appended is a table showing some of the differences of properties between the methyl-para and α - and β -methylorthoxyphenylacrylic acids.

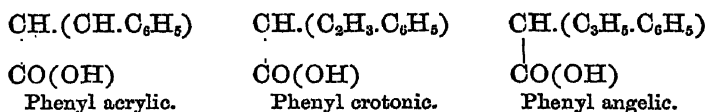
	I. Methylparoxy- phenylacrylic acid.	II. β -Methylorthoxy- phenylacrylic acid.	III. α -Methylorthoxy- phenylacrylic acid.
Fusing points	171°C.	182—183°C.	88—89° C.
Colour of ferric salt.	Brown precipitate.	Pale-brown precipitate.	Pale-brown precipitate.
„ copper „	Pale bluish-green precipitate.	Green precipitate, yellower and darker than I.	A bright yellowish-green precipitate, darker than I and II.
1 p.c. solution of sodium salt, with CaCl_2 and BaCl_2 }	A crystalline white precipitate.	—	—
2½ p.c. solution of sodium salt, with CaCl_2 and BaCl_2 }	Ditto	A white precipitate.	—
	A 2½ p.c. solution of this sodium salt deposits a large quantity of the salt on cooling in white satiny crystalline masses.	A 2½ p.c. solution of the sodium salt remains clear on cooling; the salt is only deposited on concentration, when it separates in crystals.	The sodium salt is excessively soluble in water, and, when evaporated, dries up to a gummy mass.

I have not obtained any satisfactory results by the use of valeric anhydride and a valerianate on the aromatic anhydrides, but the formation of valeric coumarin would make it appear probable that new substances may be produced in this manner.

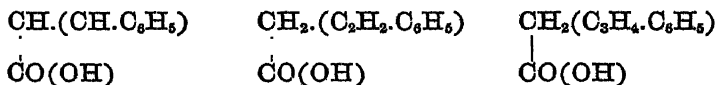
The acids described in this paper have been named as belonging to the ordinary acrylic series; those obtained by the use of acetic anhydride are certainly such, but it is doubtful if those produced with other anhydrides are strictly so. Acrylic, crotonic, and angelic acids are usually written—



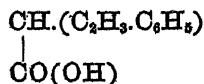
therefore the phenylated acids should be—



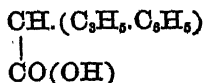
instead of which they are—



if we assume, as is most likely to be the case, that the oxygen of the aldehyde removes two atoms of hydrogen from the methyl of the propionic or butyric anhydrides, and does not attack in any way the CH_2 in union with the $\text{CO}(\text{OH})$. Fittig and Bieber (*Jahresb.* 1869, p. 584) write their phenylangelic acid thus: $\text{C}_6\text{H}_5.\text{CH}.\text{CH}.\text{CH}_2.\text{CH}_2.\text{CO}(\text{OH})$, which is the same as the above; but so long as acetic anhydride is employed true acrylic acids will of course be obtained. Thus the aldehyde of α -toluic acid (phenylacetic) should yield with acetic anhydride a true phenyl crotonic acid—

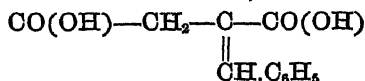


and the aldehyde of phenylpropionic acid a true phenylangelic acid—

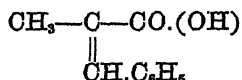


In the experiments in which I employed succinic anhydride and a succinate with benzoic aldehyde (the reaction does not take place without the succinate), the oxygen of the aldehyde must have combined with the hydrogen of one of the CH_2 groups in the anhydride (unless

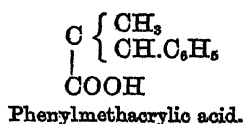
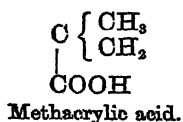
it removed one of hydrogen from each, which is not probable), and therefore at first produced a dibasic acid, constituted thus—



which, when giving up carbonic anhydride, would yield—



This acid would thus be phenylmethylacrylic or isophenylcrotonic acid—



The acids obtained with cinnamic aldehyde belong to the $\text{C}_n\text{H}_{2n} - 11\text{CO(OH)}$ series, of which phenylpropionic acid was previously the only representative.

The following is a list of the acids described in this paper, those in *italics* being previously known:—

Acids from Benzoic Aldehyde.

<i>Phenylacrylic or cinnamic</i>	$\text{C}_9\text{H}_8\text{O}_2$
<i>Phenylcrotonic</i>	$\text{C}_{10}\text{H}_{10}\text{O}_2$
<i>Isophenylcrotonic</i>	$\text{C}_{10}\text{H}_{10}\text{O}_2$
<i>Phenylangelic</i>	$\text{C}_{11}\text{H}_{12}\text{O}_2$

Acids from Cuminic Aldehyde.

Cumenylacrylic or isopropylcinnamic ..	$\text{C}_{12}\text{H}_{14}\text{O}_2$
Hydrocumenylacrylic	$\text{C}_{13}\text{H}_{16}\text{O}_2$
Hydrocumenylcrotonic	$\text{C}_{13}\text{H}_{16}\text{O}_2$
Hydrocumenylangelic	$\text{C}_{14}\text{H}_{18}\text{O}_2$

Acids from Anisic Aldehyde.

Methylparoxyphenylacrylic	$\text{C}_{10}\text{H}_{10}\text{O}_3$
Hydromethylparoxyphenylacrylic	$\text{C}_{10}\text{H}_{12}\text{O}_3$
Methylparoxyphenylcrotonic	$\text{C}_{11}\text{H}_{12}\text{O}_3$
Methylparoxyphenylangelic	$\text{C}_{12}\text{H}_{10}\text{O}_3$

Acids from Methylsalicylic Aldehyde and Coumarin.

α -Methylorthoxyphenylacrylic	$\text{C}_{10}\text{H}_{10}\text{O}_3$
β -Methylorthoxyphenylacrylic	$\text{C}_{10}\text{H}_{10}\text{O}_3$
Methylorthoxyphenylcrotonic	$\text{C}_{11}\text{H}_{12}\text{O}_3$
Methylorthoxyphenylangelic	$\text{C}_{12}\text{H}_{14}\text{O}_3$

Acids from Cinnamic Aldehyde.

Cinnamenylacrylic	$C_{11}H_{10}O_2$
Hydrocinnamenylacrylic	$C_{11}H_{12}O_2$
Cinnamenylcrotonic	$C_{12}H_{12}O_2$
Cinnamenylangelic	$C_{13}H_{14}O_2$

XII.—*Pigmentum Nigrum, the Black Colouring Matter contained in Hair and Feathers.*

By W. R. HODGKINSON and H. C. SORBY.

COLOURLESS feathers or hair dissolve completely in warm dilute sulphuric acid forming colourless solutions.

Black or dark brown feathers, &c., when so treated, yield a brown or red solution, and leave a black, amorphous substance, insoluble in acids and alkalis, and having a composition somewhat approximating to that of albumin.

These solutions in sulphuric acid give most decided absorption spectra, and by employing acid of certain strength, several distinct spectrum-giving substances may be to some extent isolated.

The feathers of the common rook are the best source of this pigmentary substance, containing about 1 per cent. In brown feathers, such as partridge-tail feathers, the amount of black pigment does not exceed 0·2 per cent.

A mean of 10 analyses of pigment from several species of <i>Corvus</i> , gave.....	C 55·4	H 4·25	N 8·5
<i>Ciconia alba</i> (mean of two) ..	55·5	4·8	8·5
<i>Corvus pica</i> („ „) ..	49·5	4·8	7·6

The composition of egg-albumin is very similar, the difference being mostly in the nitrogen and additional sulphur:—

Albumin.....	C 53·5	H 7·0	N 15·5	S 1·5
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and that the pigment is derived from albumin is not improbable.

Pigmentum nigrum is, however, with difficulty decomposed by strong acids, excepting strong nitric acid, and only slowly acted upon by bromine, forming a body soluble in water, giving absorption at the blue end of the spectrum.

It yields only traces of ammonia when ignited with soda-lime.

From the analyses the formulæ $C_{18}H_{16}N_2O_8$, or $C_9H_8NO_4$, may be deduced, but as the pigment does not appear to form any definite compound, the formulæ cannot be proved.

XIII.—*On the Corrosion of Lead by Water.*

By G. BISCHOF.

SOME eight months ago a tube was passed, in my laboratory, which is supplied with water by the New River Company, into the slate cistern, so as to act as a syphon to supply some apparatus with water. The external surface of the tube inside the cistern was therefore alternately exposed to the action of air and water, according to the level of water in the cistern.

Recently I noticed a white efflorescence on the greater part of the tube inside the cistern. An adjoining cistern of sheet lead with a lead overflow pipe fixed into the bottom shows nowhere any such corrosion. On cutting the tube it became evident that it is a composition tube, that is to say, a lead tube containing some antimony. On analysis it was found to be composed of:—

Lead	98.3
Antimony	1.7
	<hr/>
	100.0

Although the external diameter of the tube is only $\frac{1}{2}$ inch, 0.29 gram of efflorescence was obtained per foot by gentle rubbing. This dried at 100° C. contained 1.02 per cent. of sulphuric acid, corresponding with 4.1 per cent. of sulphate of lead. The remainder, excepting 1.18 per cent. of a residue insoluble in nitric acid, is carbonate of lead.

The alternate exposure to air and water appears not essential to the corrosion, as I have observed a similar effect when the same tubing remained constantly under water. The interior of the tube has also been corroded, although of course no permanent efflorescence could be formed, owing to the rapid flow of the water.

The frequent practice of plumbers of using composition tubing in connection with water-supplies is, therefore, highly reprehensible, being fraught with considerable danger to the health of those using the water for drinking or cooking.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

The Effect of Heat on Voltaic Circuits completed by an Electrolyte. By W. HELLESEN (*Compt. rend.*, lxxxiv, 83—85).—Du Moncel has shown that when one pole of an electrolyte is heated, a thermo-electric action sets in, causing a current, in which the hot pole is positive. This action may be intensified by heating the upper part of a tube filled with a solution of copper sulphate, in the interior of which a slip of copper is sealed, while a similar slip is introduced in the lower portion. The hot liquid remains at the surface and copper deposits on the upper electrode. If magnetic spirals be used, the thread of which consists of copper tubes, through one of which cold water is passed, while superheated steam is blown through the other, magnetic effects are produced, which explain the magnetic condition of the earth by referring it to its unequal temperature. If the smoky flame of a paraffin candle be used as electrolyte, and a current from 40 "Leclanché" elements, or 30 bichrome elements be passed across it, the negative wire becomes coated with a deposit of carbon, which has a tendency to arch over to the positive pole. If the two deposits be brought near each other, a series of brilliant sparks, resembling the electric light, passes between the two poles. If a long wire, rolled parallel to another on a coil, be substituted for the short wire which usually connects the interrupter of a Ruhmkorff's coil with its condenser, a strong spark, depending for its length on the size of the condenser and the nature of the insulation (mica is the best insulator) passes between the two ends of the wire, if they are kept slightly apart. It has tension enough to pass through several millimeters of air, when produced by one Bunsen's cell, a medium-sized coil, and a secondary wire 10 meters long. W. R.

Electric Conducting Power of Water. By F. KOHLRAUSCH (*Dingl. polyt. J.*, cccxii, 283—284).—The water was prepared in as pure a state as possible by distilling it from potassium permanganate, caustic potash, and potassium bisulphate, in order to destroy organic compounds and retain acids and ammonia. The product thus obtained was redistilled through a platinum condenser and collected in a platinum dish, in which the resistance was at once determined. The inner surface of this dish formed one electrode, and a smaller dish concentrically attached formed the other. The mercury-resistance of the intermediate space had been determined experimentally. Although the conducting powers (k) thus obtained varied considerably, it was never more than 1.3; the smallest value the author obtained amounted for 22° to $k \times 10_{10} = 0.72$. It cannot, however, be supposed that this

number represents the true electric conducting power of pure water, as a quick distillation increased the conducting power, probably by liquid portions being carried over mechanically, while too slow a distillation could not be allowed, as the distillate began to assume a greater conducting power, even when left for some time in the platinum dish. Although the water obtained in the above manner may represent one of the purest qualities ever prepared, it cannot be supposed that it was perfectly pure, and consequently the value $k = 0.000000000072$ cannot be regarded as more than a superior limit. Practically, however, this number undoubtedly indicates that water is a galvanic non-conductor, as we can easily estimate that a column of the above water of the length of 1mm. represents the same resistance that would be offered by a copper wire of the same diameter and of a length equal to the diameter of the moon's orbit. Commercial absolute alcohol exhibited a conducting power four times as great as that of the above water. Redistillation brought the alcohol to $k \times 10_{10} = 0.34$; ether showed $k \times 10_{10} < 0.01$.

The author gives a few examples showing how delicate an indication of the purity of water is afforded by its conducting power. By leaving it at rest in the platinum dish under a well-closed bell-jar, the conducting power of a distillate of $k \times 10_{10} = 0.77$ rose in five hours to 1.5, in twenty hours to 3.5, in eighty hours to 8.6, and in forty-four days to 30. Tobacco smoke increased its conducting power in a short time very considerably. One millioneth part of H_2SO_4 or HNO_3 (i.e. one drop in about 60 litres) increased the conducting power of the water ten times. While the conducting power of water distilled through a platinum cooler was $k \times 10_{10} = 2.4$, it was equal to 7.3 when a glass vessel was used.

Various samples of snow and rain-water gave conducting powers between $k \times 10_{10} = 4.1$ and 19.8.

These results show how it is that former observations gave higher figures for the conducting power of pure water. On the other hand, it may be perceived how convenient and sensitive a test for the purity of water is afforded by its conducting power. D. B.

Relation between the Absorbing Powers of Bodies for Heat, and their Chemical Equivalents. By M. AYMONNET (*Bull. Soc. Chim.* [2], xxvi, 535—540).—The paper describes the experimental researches and theoretical considerations which have led the author to the following conclusions:—1. The atomic absorbing power is constant for elementary substances, dissolved in the same medium, or entering into combinations chemically analogous. 2. When the temperature of a source of heat of a given kind is raised, the absorbing powers of the bodies receiving the radiations from that source are all lowered in the same proportion. R. R.

On the Rise of Temperature occasioned by passing Steam into Saline Solutions, and on the Temperature of the Vapours from Saline Solutions. By F. G. C. MÜLLER (*Deut. Chem. Ges. Ber.*, ix, 1629—1632).—It is shown that saline solutions into which steam is passed begin to boil at temperatures considerably under their

maximum boiling point, and that this maximum point is attained but slowly; also that the temperature of such boiling solutions is higher the more slowly the boiling proceeds. A thermometer placed in the vapour arising from these liquids does not register more than 100°. This is not, however, to be regarded as the true temperature of the vapour, inasmuch as in the act of condensation latent heat becomes sensible and acts upon the thermometer. M. M. P. M.

Specific Weights of Gases—Lecture Experiment. By F. G. C. MÜLLER (*Deut. Chem. Ges. Ber.*, ix, 1626).—The weight of a given volume of air may be determined by boiling a little water in a half-litre flask closed with a well-fitting caoutchouc stopper carrying a tube drawn to a fine orifice; sealing off the tube; cooling the flask with ice, and weighing; then admitting air and weighing again. If dilute sulphuric acid be employed instead of water, and if the boiling be continued until fumes of the acid begin to come off, an almost perfect vacuum may be obtained in the flask. In this case the neck of the flask must be drawn out before the experiment, and sealed off at the proper moment. Having determined the weight of a given volume of air, the weight of the same volume of any other gas may be determined by passing a current of the gas through a tared flask, closing the flask and weighing it; the difference between the weight of the flask full of air and the weight of the same full of the gas to be determined gives the weight of the latter. M. M. P. M.

On the Errors resulting from the Application of the Law of Mixture of Vapours, in the Determination of their Density. By L. TROOST and P. HAUTEFVILLE (*Compt. rend.*, lxxxiii, 975—977).—The vapour-density of certain substances has lately been determined by applying Dalton's law on the tensions of mixed gases, together with Boyle's and Gay-Lussac's laws, to a mixture of the vapour of the substance with air or even with another vapour, as in the case of Wurtz's experiments on the vapour-density of pentachloride of phosphorus. It has been shown in previous communications (*Compt. rend.*, lxxxiii, 220 and 233, also p. 33 of this volume) that the application of these laws must result in a considerable error in the vapour-density of the substance; experiments have now been made showing the extent of this error.

Known weights of silicium and carbon chlorides were introduced into a modified form of Gay-Lussac's vapour-density apparatus, and the volumes and pressures measured at 100°. As the proportion of carbon chloride was increased, the tension of the vapour of the silicium chloride diminished.

The vapour-density of the silicium chloride calculated by means of the theoretical vapour-density of the carbon chloride increased from 6.27 to 8.20, while the vapour-density of the silicium chloride, when measured in the absence of any other vapour, was found to vary only between 5.94 and 6.00.

This is the explanation of the varying densities found by Wurtz for the vapour of phosphorus pentachloride diffused in the vapour of the trichloride. Even when the vapour is mixed with air, the error is

very considerable, although of course much less than in the case of a heavy vapour. This is shown by experiments made on a mixture of phosphorus pentachloride and air, in which the calculated density varied from 6·14 to 5·15.

F. D. B.

On the Quantity of Heat absorbed by certain Substances.
By M. AYMONNET (*Compt. rend.*, lxxxiii, 971—973).—The quantities of heat absorbed by solutions of metallic salts in water, of iodine and sulphur in carbon disulphide, and of many organic liquids have been measured, and the results are given. The coefficient of atomic absorption (a) is calculated by the formula:—

$$a = \frac{AE}{DN}$$

where A = the coefficient of absorption,

E = the atomic weight.

D = the density,

N = the number of atoms.

The following table gives the values of (a) and (A):—

<i>Various Liquids.</i>	<i>A.</i>	<i>a.</i>
Sodium sulphocarbonate $\text{Na}_2\text{CS}_3\cdot\text{H}_2\text{O}$..	0·8087	3·74
Water.....	0·8020	3·61
Amyl alcohol	0·7752	3·49
Acetic acid.....	0·7281	3·43
Ethyl alcohol.....	0·6992	3·41
Methyl alcohol.....	0·6879	3·42
Chloroform	0·2516	3·36
Turpentine.....	0·5805	2·53
Toluene	0·4933	2·38
Benzene.....	0·4866	2·39

Substances dissolved in Water.

Ferric chloride	0·9829	4·32
Strontium chloride	0·9014	4·07
Acid potassium sulphate.....	0·8926	4·00
Zinc chloride	0·8591	3·99
Sodium chloride	0·8557	3·97
Zinc bromide.....	0·8423	3·93
Zinc iodide	0·8356	3·91
Barium chloride	0·8289	3·81
Ammonium nitrate	0·8221	3·71
Calcium chloride	0·8054	3·65
Water.....	0·8020	3·61
Manganese chloride	0·7852	3·47

Substances dissolved in Carbon Disulphide.

Carbon disulphide.....	0·1208	1·21
Iodine.....	0·1200	1·24
Sulphur.....	0·1185	1·18

From this table the following conclusion is drawn :—The coefficient of atomic absorption is constant: (1) for all substances dissolved in the same liquid; (2) for all substances of similar chemical constitution.

F. D. B.

Dissociation. By A. HORSTMANN (*Deut. Chem. Ges. Ber.*, ix, 1625—6).—The author's experiments were carried out with ammonium carbamate. They lead to the following results :—

1. Dissociation is not carried so far in presence of one of the products of the action, as it is in a vacuum.

2. The decrease in dissociation becomes greater as the pressure of that product of the action which remains in excess, increases; the laws regulating this decrease in dissociation may be formulated mathematically.

3. The tension-decrease of each constituent of the compound is equal for the same pressure, provided that the molecule of the compound contains equal numbers of molecules of each constituent (sal ammoniac, for instance).

4. If, on the other hand, more molecules of one constituent are present in the compound than of the other (ammonium carbamate, &c.), then the action of each constituent varies, dissociation being decreased to a greater extent by the presence of that constituent, the largest number of molecules of which are present in the compound.

5. Dissociation is decreased by the same constituent in the same proportion at all temperatures, provided that the pressure exerted by the constituent in excess stands in the same proportion to the dissociation-tension *in vacuo* as corresponds with the temperature of the experiment.

M. M. P. M.

On the Soft and Semi-fluid States of Aggregation. Regulation and Recrystallisation. By L. PFAUNDLER (*Wien. Akad. Ber.*, lxxiii, 249—266).—This paper consists of four divisions. In the first of these, the author discusses the definition and classification of semi-solid bodies, which he divides into three classes—(1) plastic bodies; (2) really soft bodies; and (3) mixtures of these two groups. He defines a body as soft, when it undergoes a change of form by bending, pressure, or tension, without breaking or tearing, and will retain its new form after the cessation of such force. Should the change of form be produced by the weight of the body itself, it is called semi-fluid, but no great distinction can be drawn between the two conditions of soft and semi-fluid. Plastic bodies the author classifies as those bodies which are soft by virtue of being mechanical mixtures of small solid particles with particles in the state of what he calls real fluidity, as for instance, wet clay. These bodies are characterised by the possibility of a mechanical separation, so that the degree of softness cannot be actually changed by temperature, but only by the different proportions of the component parts. Real soft bodies he describes as homogeneous, and as divisible into two separate groups, namely: (1.) Simple chemical substances, as phosphorus, or pure combinations, as ice, &c; and (2.) Intimate mixtures

(perhaps molecular combinations) of solid bodies, or of solids with liquids, as mixtures of resin or resin with turpentine, oil, &c.

The second division consists of hypotheses on the occurrence of melting, and on the existence of semi-fluid conditions. In this, the author considers (1) the process of melting; (2) the perfectly soft condition; (3) the temperature of softening, melting, and solidifying; (4) the phenomena of bending of soft bodies; and (5) the adhesion of soft bodies.

With regard to the process of melting, the author thinks the ideas previously held on this point to be imperfect: for, according to these notions, should heat be applied, say, to a piece of phosphorus, if all the molecules were similar in material as well as in position and conditions of motion, the gradually-introduced heat would only raise the temperature of all the molecules up to the melting point. From this point, should further heat be added, it can melt only the molecules nearest to the source of this heat. If, now, we introduce only a portion of the heat necessary for melting the whole body (the body being isolated from external heat), we should then have a piece of solid and a quantity of liquid phosphorus both at the melting point. The true conditions of melting, however, the author thinks to be carried on in a different manner, as this pre-supposed similarity of molecular conditions cannot be arrived at, especially in the case of amorphous bodies, which he regards as irregular and different; he also considers that the temperature of the molecules is always different and changing, the total temperature remaining the same so long only as no fresh heat is introduced. If, now, heat is applied gradually, the mean temperature rises, and at last a point is reached when the molecules which have attained their highest activity leave the solid and assume an increasing motion in the liquid state. With regard to the "soft condition," the author says that the body is first soft and then semi-fluid, and that bodies in the so-called soft state of aggregation, are mixtures of solid groups of molecules with liquid ones, that is to say, moving molecules which are constantly changing places with the solid ones.

With regard to regelation and recrystallisation, after mentioning some of the arguments used by Faraday, Forbes, Tyndall, Helmholtz, and others, the author goes on to state that his present ideas (*Wien. Akad. Ber. Bd., lix*) are nearly identical with those which he held formerly, and bear the same relation to the theories advanced by J. and W. Thomson and Helmholtz.

The two opinions can stand side by side; regelation could still be possible, according to the author's theory, where no pressure is at hand, or where this (as in the case of other bodies besides ice) produces no lowering of the melting point. The latter, furthered by the ice melting, increases also the number of the fluid molecules and must, therefore, help the action of regelation. A pull, instead of pressure, acts in an opposite manner, thus impeding the change; therefore, perhaps, the only point of contradiction which appears to exist between the experiments of these physicists and the author's present theory may be withdrawn, viz., that regelation can be brought about only through pressure and not by tension. The explanations

which the author attempts in this paper have, he says, one and the same principle for their foundation, namely, what he calls "the variation of separate molecules, and through that the possible concurrence of the same." He has already shown (*Pogg. Jubelband*, 182) that this principle may be brought into close relation to the principle of natural science, which he terms the struggle for existence (*Kampf ums Dasein*). This shows itself most plainly in the phenomena of bending in soft bodies and of regelation; if the molecules of a body be brought into a crushed position or strained circumstances by external influences,—variation, concurrence, or agreement, enable it to conform to these circumstances or position. The most important molecules under these conditions, are those which are most freely movable; by their means, the position of the molecules which are crushed to the greatest extent is determined, and they can be replaced by others more favourably situated in the mass. The changeability and mobility made possible by the variation of the molecules, and the property of fitting and conforming thereby brought about, the author believes to play a most important part in the unorganised, as well as in the organised world. He suggests that physiologists might find in this transference of molecules the explanation of the changing of organs in suiting themselves to new circumstances and new functions. He brings forward the idea that the motion of molecules is brought about as if they were conscious of a purpose, or led by one common idea; this, of course, he only suggests, but considers that they seem to follow one law, that of the increase of entropy.

J. M. T.

The Application of the Principle of Dissimilar Molecules to the Explanation of the Phenomena of Supersaturated Solutions, Superfused Bodies, Spontaneous Explosions, and the Gradual Crystallisation of Amorphous Bodies. By L. PFAUNDLER (*Wien. Akad. Ber.*, lxxiii, 2te Abth. 574—583).—In the commencement of this paper, the author refers to the ideas promulgated in his former paper, published in the same journal (*Wien. Akad. Ber.*, lxxiii), bearing considerably on the questions he raises in the present communication. (1.) With regard to the solidification of supersaturated solutions, he thinks that before a crystal can be formed in one of these solutions, a certain number of molecules must be below the temperature at which the crystals begin to form, the time occupied before this takes place being directly proportional to the strength and temperature of the solution. For instance, before a crystal of sodium sulphate can be formed in a supersaturated solution, a quantity of the molecules "which are, at all events, partially dissociated in the solution," must meet in such a manner as not only to form the compound $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, but also with so little energy and in such a state of aggregation, as to form and remain as a "crystal molecule." The author takes into consideration supersaturated solutions of gases, which he thinks have been proved to exist. In these, he considers that when a solution or liquid is heated, before ebullition can take place, certain molecules attain a critical point, at which they move freely to and fro in the

liquid without the formation of bubbles till several meet. In this case, he entertains the idea that a liquid at the boiling point, without bubbles, may have a higher boiling point than when the evolution of bubbles takes place. With regard to the gradual transformation of bodies from the amorphous to the crystalline state, the author considers that the former is necessarily not so stable a condition as the crystalline; in all bodies, difference of temperature occurs, when, in amorphous bodies, certain molecules will move more freely than others, as in the case of the gas-molecules in supersaturated gas solutions; these, he thinks, will gradually assume the crystalline form, this transformation eventually extending through the whole mass, and being materially assisted by external shocks, &c., as in the case of steel anvils, &c. The author concludes with the supposition that the reasoning concerning this gradual change from amorphous to crystalline structure may find application in certain geological changes.

J. M. T.

On Supersaturated Saline Solutions. By J. G. GREENFELL (*Proc. Roy. Soc.*, xxv, 124).—The author has made many experiments by placing drops of the solutions on different surfaces in various positions, and from the results he draws the following conclusions:—

1. Exposure to air and dust has no effect on some supersaturated solutions.

2. The sulphates are the most sensitive. Exposure of a clean glass plate for half-an-hour to the air of the laboratory, caused nearly all the drops of sodium sulphate put upon it to crystallise at once, whilst the same plate, recently cleaned, is quite inactive.

3. Even the sulphates are unaffected by the dust of the open air, and generally by that of ordinary rooms.

4. Anhydrous salts, or modified salts, sometimes new, are produced by the spontaneous evaporation of the solutions in drops.

5. Drops can be rapidly touched on their surface with crystals of the same salt without crystallising.

6. Greasy surfaces, whether films or lenses, have no effect.

7. The shape of the vessel has, sometimes, a material influence on the possibility of obtaining a supersaturated solution.

8. Air and dirty surfaces are active on salts which apparently cannot exist in air.

9. Scratching a hard surface will cause a particular solution to crystallise.

The author, also, made experiments on hyperacid sodium sulphate, $\text{NaH}_2(\text{SO}_4)_2$, and on the solubility of decahydrated sodium sulphate in water.

He finds that when this latter salt is added, little by little, to water, at 39° , it is possible to dissolve 600 parts of salt in 100 of water, and when the solution is heated, very little salt is deposited, until a temperature of 70 — 80° is reached, when a copious precipitate is suddenly formed, as if it had been the 10-atom salt in solution at first, which underwent dissociation at a temperature of about 80° .

C. W. W.

Molecular Volumes of Sulphates and Selenates. By O. PETTERSSON (*Deut. Chem. Ges. Ber.*, ix, 1676—1678).—The molecular volumes of crystals obtained from mixtures of sulphates and selenates were calculated from analyses showing the proportion of sulphuric to selenic acid. The magnitude of the number expressing the molecular volume seems to rise and fall with the greater or less proportion of selenic acid in the compound. The author throws out the suggestion that the isomorphism of selenates and sulphates arises from an internal inter-crystallisation of the molecules. G. T. A.

Lecture-experiment to show the Increase of Weight on Burning a Taper. By VICTOR MEYER (*Deut. Chem. Ges. Ber.*, ix, 1666—1668).—A taper is fixed at the bottom of a lamp-glass suspended from one arm of a balance, and containing pieces of caustic soda at the upper part, kept in place by wire-gauze. The apparatus is counterpoised either by a weight or by a similar arrangement in which the taper is not lighted. G. T. A.

Behaviour of Palladium in an Alcohol-flame. F. WÖHLER (*Deut. Chem. Ges. Ber.*, ix, 1713—1715).—On heating palladium in the form of sponge or foil in a flame of alcohol or coal-gas, it becomes coated with a thick layer of soot, forming a spongy mass. On burning this away, the palladium remains as a skeleton, even when foil has been used, and is quite brittle.

Spongy palladium does not act on ethene at 100°, or any temperature below red heat, but at this temperature carbon separates out, and hydrogen is formed, although without using palladium the ethene was not changed. On marsh-gas, palladium does not act at all. When palladium is fused in a carbon crucible, it does not take up any carbon, and the above phenomena are probably due to the peculiar action of hydrogen on the metal. In conclusion, an apparatus is described, by which the occlusion of hydrogen by palladium can be easily shown. C. S.

Note on a Manometric Apparatus, with reference to a Recent Paper by M. Cailletet. By MIGNON and ROUART (*Compt. rend.*, lxxiv, 183).—This apparatus is composed of an iron or steel reservoir containing mercury, and a glass tube indicating the movements of the liquid, the two parts of the apparatus being connected by an adjustable joint.

If the manometer is for low pressures, the reservoir is oval and made of thin metal, but if the apparatus is for high pressures the reservoir is circular and very thick; the pressure acts from the interior, and the indicating mercury is placed in an exterior envelope. In this class of apparatus temperature plays an important part, for the heat and the pressure both tend to raise the mercury in the gauge, but in many cases these two effects need not be separated, as for instance in measuring the tensions of vapours.

This apparatus, however, can be made to separate perfectly the effect of heat from that of pressure. This is done by placing in the

mercury an indifferent substance, such as glass, porcelain or metal, which by its expansion balances the expansion of the mercury and the vessel containing it.

C. W. W.

Inorganic Chemistry.

Does Ozone combine with Free Nitrogen in Presence of Alkalis to form Nitrites and Nitrates? By M. BERTHELOT (*Compt. rend.*, lxxxiv, 61—64).—Schönbein stated in 1849 that this reaction takes place in presence of lime-water. But Schönbein's lime contained a considerable quantity of nitrates; he was correct in his statement, provided the ozone was prepared by slow oxidation of phosphorus. In Berthelot's experiments, ozone prepared from oxygen by the electric discharge did not oxidise nitrogen in presence of chemically pure baryta-water; but air ozonised by phosphorus yielded a trace of nitrate, less than $\frac{1}{10}$ of a milligram. It appears therefore, that Schönbein was correct in stating that nitrous compounds are formed during oxidation of phosphorus, but free ozone yields hardly a trace in presence of alkalis and nitrogen.

W. R.

Synthesis of Water: Lecture Experiment. By F. G. C. MÜLLER (*Deut. Chem. Ges. Ber.*, ix, 1627—1628).—The orifice of a Daniell's burner for the oxyhydrogen flame is passed through a cork into a bottomless test tube, the lower part of which is drawn out, and passes through a cork into one limb of a U-tube. To the other limb of this tube is attached a piece of glass tubing bent twice at right angles and dipping under water.

The Daniell's burner communicates with gasometers containing oxygen and hydrogen: the gases are ignited, the apparatus is adjusted, the U-tube being surrounded with cold water, and the outflow of the gases is regulated so that no bubbles of gas escape from the U-tube. The water produced is weighed, and the volumes of hydrogen and oxygen used are read off from the indicators in the gasometers.

Other gases may be burned in the apparatus, and the products absorbed by suitable means. The combustion of ethylene, or of carbon monoxide, is an interesting lecture experiment. The carbon dioxide is absorbed in a tube containing soda-lime and calcium chloride, and communicating with the U-tube.

M. M. P. M.

Apparatus for Demonstrating the Manufacture of Sulphuric Acid. By K. HEUMANN (*Deut. Chem. Ges. Ber.*, ix, 1737—1738).—The sulphur is burned in a porcelain boat, which is inserted into a short glass-tube, through which a current of air is passed by an aspirator. The mixture of sulphur dioxide is then passed through a glass-cylinder filled with coke, and then successively through three large glass-globes, the first of which contains a small basin with nitric acid. The three globes are provided with tubes for passing steam into the sulphuric acid formed, which then runs back into the cylinder,

which acts as a Glover's tower. The gases escaping from the last globe pass through a second cylinder (Gay-Lussac) filled with coke, over which sulphuric acid runs and then enter a glass-bulb to show that all nitrous fumes are removed. C. S.

Action of Dry Gaseous Hydrochloric Acid on Sulphates at Various Temperatures. By C. HENSGEN (*Deut. Chem. Ges. Ber.*, ix, 1671—1676).—Potassium sulphate (K_2SO_4) is not acted on by dry gaseous hydrochloric acid till the temperature rises to 100° , and complete decomposition does not take place till a dull red heat is reached, when sodium chloride and sulphuric acid are formed.

Anhydrous sodium sulphate is acted on in the same way, but a still higher temperature is needed. Hydrated sodium sulphate ($10H_2O$) on the other hand is converted into sodium chloride by a stream of hydrochloric acid gas at ordinary temperatures, and even at -17° the decomposition takes place, though slowly.

Anhydrous lithium sulphate (Li_2SO_4) behaves like the corresponding alkaline sulphates, but $Li_2SO_4 + H_2O$ is decomposed at ordinary temperatures.

Calcium, barium, and strontium sulphates are all nearly completely decomposed at a dull red heat. Anhydrous copper sulphate ($CuSO_4$) is rapidly attacked by the gas, and appears to form an addition-product, $CuSO_4 + 2HCl$. In dry air over caustic soda this body passes into the anhydrous sulphate, but in ordinary air it first becomes greenish and then forms the five-atom blue salt. The sulphate is either not attacked at all or only very slightly by hydrochloric acid gas at a strong heat. The hydrate, $CuSO_4 + H_2O$, behaves in the same way as the anhydrous salt. Possibly in this case the reaction is $CuSO_4 \cdot H_2O + 2HCl = CuSO_4 \cdot H_2Cl_2 + H_2O$.

In the case of the anhydrous sulphate one might suppose such a decomposition as the following to take place, $CuSO_4 + 2HCl =$

$Cl-Cu-O-SO_2 \begin{matrix} \nearrow Cl \\ \searrow (OH)_2 \end{matrix}$, analogous to the formation of chloro-

chromic acid. No doubt the body formed by the anhydrous sulphate and hydrochloric acid plays an important part in the production of chlorine by Deacon's process. G. T. A.

Dissociation of Sodium Bicarbonate at 100° . By V. URBAIN (*Bull. Soc. Chim.* [2], xxvi, 440, 441).—Bicarbonate of sodium enclosed in a flask and maintained at the temperature of 100° , does not undergo decomposition. If, however, a current of air be made to pass through the flask, decomposition takes place with rapidity. This is a case of *dissociation*, and, as usual, the decomposition cannot proceed unless the gaseous products are removed, or their tension kept below the tension of dissociation of the compound, which for sodium bicarbonate at 100° , is about 22 centimeters. These facts are pointed out in relation to the views held by A. Gautier on the decomposition of alkaline bicarbonates in blood (see *Chem. Soc. J.*, 1876, ii, 602). The author, in opposition to Gautier, maintains that when the dried plasma is subjected to a temperature of 100° , the sodium bicarbonate is not

decomposed, each particle being enclosed as by a varnish, and therefore under the same conditions as the salt in the closed flask. He cites in support of his position direct experiments with powdered bicarbonate to which albumin, gum, or sugar had been added.

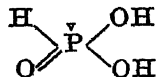
R. R.

Note on a Crystallised Compound of Salt and Water. By E. BEVAN (*Chem. News*, xxxv, 17).—Sodium chloride crystallised from its solution in hydrochloric acid, deposits crystals having the percentage composition $\text{NaCl} = 94.5$, $\text{H}_2\text{O} = 5.48$.

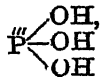
These contain only a slight trace of hydrochloric acid, and break up after a short time into the anhydrous salt and water.

E. W. P.

Composition of certain Phosphites. By AD. WURTZ (*Compt. rend.*, lxxxiii, 937—940).—The question whether phosphorous acid should be represented by the first or the second of the following formulæ:—



Unsymmetrical.

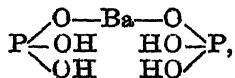


Symmetrical.

having lately come under discussion, the author is induced to publish analyses of the following salts, which were made in his laboratory in 1869.

These analyses show that calcium phosphite is expressed by the formula PHCaO_3 ; neutral barium phosphate by PHBaO_3 ; acid barium phosphite by $\text{P}_2\text{H}_4\text{BaO}_6$.

This last salt the author represents by the constitutional formula—

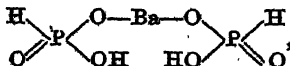


derived from symmetrical phosphorous acid, which contains trivalent phosphorus.*

F. D. B.

Action of Calcium Sulphate on the Sulphates of the Alkalis. By A. DITTE (*Compt. rend.*, lxxxiv, 86).—Gypsum, in fine powder, combines directly with potassium sulphate, to form small white nacreous plates, themselves composed of groups of fine transparent

* It might, however, be equally well represented by the formula—



derived from unsymmetrical phosphorous acid. The phosphorous ethers afford examples of both modifications, viz., symmetrical ethers formed by the action of $\text{P}(\text{OH})_3$ on alcohols, e.g., $\text{PCl}_3 + 3\text{C}_2\text{H}_5\text{OH} = 3\text{HCl} + \text{P}(\text{OC}_2\text{H}_5)_3$; and unsymmetrical ethers formed by oxidation of primary phosphines, e.g., $\text{P}(\text{C}_2\text{H}_5)_2 + \text{O}_2 = \text{C}_2\text{H}_5\text{P}(\text{OH})_2$.—[Ed.]

prismatic needles radiating from the same point. The reaction takes place more slowly with artificially prepared calcium sulphate, or with anhydrite. The formula of the double salt is $2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. It is decomposed slowly by water.

If a little sulphuric acid be added to the mixture of the two sulphates, the calcium sulphate is deposited, and after standing for 48 hours is converted into flat transparent prisms, of the formula $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. These crystals lose their water, and become dull when heated.

Calcium sulphate combines in similar circumstances with rubidium sulphate, to form transparent needles grouped in stars. Their formula is $2\text{CaSO}_4 \cdot \text{Rb}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.

Ammonium sulphate also combines to form long four-sided needles, decomposed immediately by cold water, of the formula $\text{CaSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$. Neither sodium, lithium, magnesium, nor thallium yield double salts.

W. R.

Preparation of Lithium Carbonate and some New Compounds of Lithium from Lepidolite. By F. FELSINGER (*Arch. Pharm.* [3], viii, 198—219).—After recapitulating the various processes by which pure lithium salts may be prepared from lepidolite, the author criticises them. None answered his purpose, which was to prepare lithium salts on a large scale for commercial purposes, *e.g.*, for use in photography, in pyrotechny, &c. His own process is as follows:—

The lepidolite, reduced to fine powder, was treated with strong sulphuric acid containing some nitric acid, in a large brick trough, at a gentle heat. It was heated with constant stirring till it gained consistency enough to be made into balls, which could be easily introduced into a reverberatory furnace. The slight excess of sulphuric acid was driven off at a gentle heat, the temperature was then raised, and the pieces while still hot were treated with water in vessels lined with lead. The residue consisted of almost pure silica, for which a market is easily found. As lithium does not replace potassium in alum, a sufficient quantity of potash is added to transform all the sulphate of aluminium present into alum. On evaporation the alum separates in powder. It is removed, dried in a centrifugal machine, and on recrystallisation is obtained in fine crystals. The excess of alumina is then precipitated from the mother-liquor by milk of lime, and the excess of sulphuric acid by barium chloride. The barium sulphate obtained is a marketable article. The liquid is then evaporated, and the mixed chlorides of lithium, potassium, sodium, calcium, and sometimes barium, exhausted with absolute alcohol. The lithium and calcium chlorides are dissolved. The calcium is separated as oxalate, and the lithium chloride evaporated and crystallised. It is precipitated with ammonium carbonate and ammonia, and brought into the market in the form of carbonate. The advantages of this process are complete consumption of the crude material; cheap reagents; common plant; precipitates which are easily washed, and a number of marketable chemicals, *e.g.*, silica, alumina, potash alum, and lithium carbonate.

Borates of Lithium.—Of these the author has prepared three. The

first was prepared by boiling equivalents of boracic acid and lithium carbonate till carbonic anhydride was no longer evolved. On treatment with alcohol it was obtained as a granular precipitate. Its formula is $\text{Li}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O}$. Even with excess of lithium carbonate no less acid salt was obtained. It lost two equivalents of water at 200° . The second salt was prepared by saturating one equivalent of boracic acid with lithium carbonate, and adding another equivalent of acid. It was precipitated with alcohol. Its formula is $\text{LiB}_3\text{O}_5 + 3\text{H}_2\text{O}$. Under the microscope it had a crystalline appearance. The third salt was prepared by boiling lithium acetate with boracic acid till all acetic acid was expelled, and evaporating over sulphuric acid. Crystalline crusts deposited, of the formula $\text{Li}_2\text{B}_6\text{O}_{13} + 10\text{H}_2\text{O}$. The author was not successful in preparing a more acid salt than the last described; such salts might, however, be probably formed by use of lithium hydrate. The flame reaction of $\text{Li}_2\text{B}_4\text{O}_7$ shows only that of the base; the second gives a flame with green border; while the third exhibits the colours both of base and acid. Sulphuric acid separates boracic acid from dilute solutions of the second and third, but not from the first. W. R.

Crystallised Barium Silicate. By F. PISANI (*Compt. rend.*, lxxxiii, 1056—1058).—In several laboratory bottles in which solution of barium hydrate had remained for five years, the author found well-defined transparent crystals attached to the sides of the vessels. The crystals fused to a white enamel when heated, giving off water. They were scarcely soluble in cold water, but dissolved in a large quantity of boiling water. The angles of the crystals were measured, and their optical properties examined. Their form is an orthorhombic prism of $97^\circ 4'$, having the dimensions $b : h :: 1000 : 282.6$; $D = 749.3$; $d = 662.2$. Their chemical composition corresponds with the formula $\text{Ba}_3\text{Si}_2\text{O}_4 + \text{H}_2\text{O}$. R. R.

Crystals of Gallium. By LECOQ DE BOISBAUDRAN (*Compt. rend.*, lxxxiii, 1044).—A mention of crystals of gallium presented to the Academy of Sciences. The crystals have the form of well-defined octohedrons, truncated at the base. Their faces are not sufficiently flat to allow of exact measurements; but the values found for the angles appear to lead to a clinorhombic form. R. R.

On the Capacity of Saturation of Manganous Acid. By A. GOURGEU (*Compt. rend.*, lxxxiv, 177).—In a previous research the author was unable to fix more than one-fifth of an equivalent of alkali on 1 eq. of hydrated manganese dioxide; but subsequently Weldon formed a manganite of equal proportions of acid and base.

On treating an aqueous solution of potassium manganate with carbonic acid, potassium hypermanganate is formed, and a precipitate deposited which gives 17.2 per cent. of potash, a proportion very near that (17.8) required by the formula $(\text{MnO}_2)_6\text{K}_2\text{O}$. If very dilute solutions of potash are used instead of water for washing this precipitate, bodies having the formula $(\text{MnO}_2)_4\text{K}_2\text{O}$ and $(\text{MnO}_2)_3\text{K}_2\text{O}$ are obtained. As these results showed that alkaline manganites are decomposed by

water, and as the barium and calcium salts were found to be equally unstable, the author made and analysed the manganite of manganese.

A mixture of caustic potash with excess of a manganous salt was shaken in a flask. At the end of a fortnight the precipitate had acquired a brown colour, which was not changed on exposure to the air. After washing, the precipitate contained neither potash, carbonic acid, nor sub-salt of manganese, and did not yield manganous oxide to ammoniac chloride. Treated with nitric acid it split up into monoxide, which dissolved, and black hydrated dioxide, which remained undissolved. Analysis showed that it contained 2.5 per cent. of water in combination, and that the anhydrous substance contains 7.17—7.28 per cent. of oxygen more than the protoxide, being evidently the same as the red oxide $3(\text{MnO}_2)$ or $\text{MnO}_2 \cdot 2\text{MnO}$, which contains 6.97 per cent. This body is therefore *bibasic manganese manganite*. When formed by means of potash it is amorphous, but if ammonia is used instead of potash it has a clear chocolate colour, and a crystalline appearance.

Several of the higher oxides of manganese form true hydrates with water, containing, when dried in the air, from 3.5 to 27 per cent. of water, and when dried in a vacuum from 2.7 to 7.5 per cent. Treated with dilute solutions of soda, they retain $\frac{1}{10}$ to $\frac{7}{10}$ per cent. of alkali, those containing the largest amount of water absorbing the largest amount of alkali.

C. W. W.

Physical and Chemical Properties of Ruthenium. By H. STE. CLAIRE DEVILLE and H. DEBRAY (*Compt. rend.*, lxxxiii, 926—932).—Unlike osmium, which has formed the subject of previous communications (*Chem. Soc. J.*, 1876, ii, 279), ruthenium, when heated in oxygen, forms an oxide, RuO_2 , which does not sublime at a red heat. To obtain ruthenium tetroxide, RuO_4 , the metal when freed from osmium is treated with potash and saltpetre, and the solution of ruthenate thus formed is saturated with chlorine and distilled on a water-bath in a current of this gas. Yellow crystals of ruthenium tetroxide then pass over, by the reduction of which pure ruthenium is obtained. The solution of the tetroxide in potash, when heated with alcohol, yields the dioxide, which is reduced with coal gas. The metal is then alloyed with 5 or 6 times its weight of pure tin, and the alloy freed from excess of tin with hydrochloric acid. Thus prepared it consists of equivalent quantities of tin and ruthenium, and crystallises in modified cubes. From the pure alloy, ruthenium is separated by heating in a current of hydrogen chloride. The metal thus obtained has a density of 12.261 at 0° .

When the ruthenate of potash is being saturated with chlorine, the liquid becomes dark green, and filled with small black crystals, which when separated are found to be isomorphous with permanganate of potash. They decompose rapidly, forming ruthenium oxide and the orange ruthenate. Analysis showed them to consist of $\text{Ru}_2\text{K}_2\text{O}_4$. Heated in a current of hydrogen, these crystals give off water; they are also decomposed by chlorine.

The analysis of ruthenium alloys is carried out as follows:—0.5 gram of the substance is heated to redness with 2 grams of saltpetre

and 5 grams of potash in a gold crucible. After cooling, the contents are dissolved in water, and the crucible washed out with sodium hypochlorite. The whole is then placed in a flask and saturated with chlorine, and finally heated to 80° on a water-bath while a slow current of chlorine is passing through. The excess of the gas, together with the ruthenium tetroxide which it carries over, is absorbed by a solution of potash; the liquid in the flask is then rendered alkaline, and the saturation with chlorine repeated until the solution no longer becomes dark green during the operation. The solution of potash is now treated with alcohol, which precipitates the ruthenium as oxide; this is washed, and reduced by pure hydrogen. The whole method is explained in detail.

F. D. B.

Mineralogical Chemistry.

Simultaneous Formation of Zeolites (Chabasite and Christianite) under the Influence of Hot Springs, in the Neighbourhood of Oran, Algeria. By DAUBRÉE (*Compt. rend.*, lxxxiv, 157).—Minute crystals were observed lining cavities in masses of brick and mortar obtained from Oran. These crystals did not effervesce with acids, and under the microscope appeared to be of two distinct species. They were transparent, colourless, and had a perfect lustre.

The first species was a right four-sided prism, terminated by a tetragonal pyramid, whose four faces rested on the edges of the prism. It resembled in every respect the mineral known as *christianite* or calcareous harmotome; its angles also are the same as those of the latter mineral.

The faces of some of the crystals are marked by crossed striations, indicating the twinned character of the species; in others this character is exhibited by re-entering angles.

The other crystals are terminated by rhombohedrons whose angles approach 90° , like chabasite. The rhombohedrons are joined in pairs, or have striated faces, as often happens with these crystals in nature. Some of the crystals of both species are nearly a millimeter long.

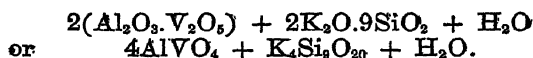
C. W. W.

On two new Vanadium Minerals. By H. E. Roscoe (*Proc. Roy. Soc.*, xxv, 109).—*Roscoelite*. This mineral was found in a gold-mine at San Francisco, and serves as a matrix for gold. It occurs in radiating and foliated talc-like masses, filling cavities in a schistose porphyry. It is of a greenish-grey colour, opaque when seen in mass, but translucent in thin splinters. Lustre subvitreous to fatty; hardness about equal to that of talc; specific gravity = 2.902.

Two analyses gave the following results:—

	SiO ₂	V ₂ O ₅	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	H ₂ O
I	41.25	28.85	14.34	1.04	1.45	1.96	.61	8.25	.72	.94
II		28.86	13.94	1.23	0.85	2.06	.62	8.87	.92	1.22
Mean ..	41.25	28.60	14.14	1.13	1.15	2.01	.61	8.56	.82	1.08

From these figures the following formula was deduced, a portion of the alumina being replaced by the sesquioxides of iron and manganese, and a portion of the potash by lime, magnesia, and soda :—

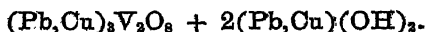


Mottramite.—This mineral occurs as a crystalline incrustation on Keuper sandstone at Alderly Edge and at Mottram St. Andrews, in Cheshire. The incrustation is usually very thin, 3 or 4 millimeters at the most; occasionally masses of the size of a walnut have been found. Sometimes the mineral has a black velvety appearance, and consists of numerous minute crystals, which are black by reflected light, but are sub-translucent, and transmit yellow light in thin particles. The compact mineral is purplish-brown and opaque. Lustre resinous; streak yellow; hardness of compact portion about that of calc-spar, sp. gr. = 5.894.

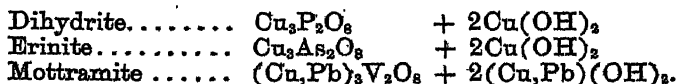
Analysis gave the following numbers :—

	V_2O_5 .	PbO.	CuO.	Oxides of Fe, Zn, Mn.	CaO.	MgO.	H_2O .	SiO_2 .
I	16.78	50.49	19.72	2.52	2.61	0.37	3.63	0.87
II.....	17.49	51.45	18.48	2.52	1.64	0.16	3.63	1.25
Mean ..	17.14	50.97	19.10	2.52	2.13	0.26	3.63	1.06

from which the following formula was deduced :—



Mottramite is interesting as forming the third term in a second (doubtless) isomorphous group of phosphates, arsenates, and vanadates, corresponding with the well-known pyromorphite, mimetesite and vanadinite group. The new group is :—



C. W. W.

Composition of "Touchstone." By E. DUMAS (*J. Chim. Pharm.* [4], xxii, 426—428).—A specimen of touchstone which had done good service in the Assay Office, and was, probably, a portion of the specimen examined by Vauquelin, was analysed by MM. Mermet and Delachanal, with the following results :—

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO.	MgO.	K_2O .	Na_2O .
81.40	5.25	1.15	0.43	0.13	0.69	1.70
P_2O_5 .	S.	H_2O .	C.	H.	N.	Loss.
9.05	0.6	0.7	4.37	0.09	0.19	0.25 = 1006.0
Organic matter.						

Dumas, who has paid considerable attention to the constitution of minerals commonly known as "touchstones," considers them to be a variety of fossil wood, in which a small portion of the woody tissue still remains unreplaced by silica. He bases his opinion principally upon the fact that certain specimens of touchstone from the Alps, which yield on ignition an ash consisting entirely of silica, retain in their mineralised condition the form of branches or trunks of trees, with characters sufficiently well marked to enable even the genus of the tree to be determined. The microscopic examination of thin sections of touchstone by Dr. Renault has further shown that in some of these minerals, at least, the organic matter consists of a sort of bitumen resulting from the transformation of the tissues of the primitive wood, and that, on account of the deep colour of the bituminous matter which fills the spaces originally occupied by the cell-walls and fibres, it is possible to distinguish the form and details of these cells as they lie embedded in the siliceous matrix. The vegetable origin of touchstone appears, therefore, to be clearly demonstrated. J. W.

Crystals of Magnetic Oxide of Iron formed in roasting a Spathic Mineral. By BOUSSINGAULT (*Compt rend.*, lxxiii, 1007, 1008).—Regular octohedral crystals, magnetic without polarity, and having the composition of natural magnetic iron oxide, Fe_2O_4 , were found imbedded in a crust of crystalline oligiste, on the walls of a kiln (at Ria, Pyrénées-Orientales), on which a spathic iron containing carbonates of manganese and of calcium, and a gangue of quartz, had been roasted. R. R.

Analysis and Determination of the Fusibility of three Bavarian Felspars. By CARL BISCHOF (*Ding. polyt. J.*, cccxii, 265—271).—The laws and relations between pyrometric and analytical results in estimating various felspars which were pointed out by the author in *Dingl. polyt. J.*, 1875, ccxvii, 319, and this Journal (1876, i, 527), receive further confirmation from the following investigations:—

1. *Felspar from the Fichtelgebirge of Arzberg.*—This felspar consists of a crystalline mass having the characteristic foliated structure, white colour, and vitreous lustre, with a yellowish-grey tinge. An average sample carefully prepared from one kilo., of the mineral, and affording a white powder with a slight greyish tinge, was found to fuse completely at the melting-heat of platinum. At a lower temperature, at which a cast-iron splinter begins to fuse, the spar is softened to an externally vitreous, and internally completely vitrified mass, which appearance characterises this felspar as a comparatively fusible mineral, in which respect it is identical with the Bohemian and the Odenvald spars mentioned in the former paper.

Analysis of a dried sample gave:—

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	
70.10	17.16	0.91	0.45	0.98	1.52	8.65	= 99.77 per cent.

This spar, with its large amount of silicic acid, and a proportionately large quantity of magnesia, belongs to the soda-felspars (albites), the

chemical formula of which, when calculated, gives numbers differing but slightly from the normal proportion of the calculated double silicate:— $1 : 2.75 :: 12.41 \text{ NaO}, \text{SiO}_3 + \text{Al}_2\text{O}_3, 3\text{SiO}_3$ (instead of $1 : 3 :: 12$). The chemical composition, if calculated (as previously described) like that of fire-clays, gives $0.83(\text{Al}_2\text{O}_3, 4.68 \text{ SiO}_3) + \text{RO}$, or, according to the law already established regarding the fusibility of felspars, $0.83 \times 4.68 = 3.88$, a number which is comparatively very high, and corresponds with the empirical results.

2. *Felspar from the Oberpfalz at Weiden*.—A yellow rock with brown spots, and interspersed here and there with mica and quartz. When heated very strongly it behaves like the spar above described, but does not soften at a lower temperature, and under the microscope merely shows slight indications of fusion. This spar, therefore, belongs to the category of difficultly fusible felspars. Analysis gave:—

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
65.49	19.44	0.59	0.86	0.89	1.95	10.17

= 99.39 per cent.

It belongs to the albites. Its chemical formula, $1 : 2.60 :: 9.82$, shows that a considerable portion of the silica must have been carried away by processes of decomposition. Its composition calculated like that of the clays, gives $0.82(\text{Al}_2\text{O}_3, 3.86 \text{ SiO}_3) + \text{KO}$, or $0.82 \times 3.86 = 3.17$, a result agreeing with the law that the fusibility increases with the number obtained by this method of calculation.

3. *Felspar from the Oberpfalz at Tirschenreuth*.—Slightly bluish-white mineral. Its cleavage-surface exhibits laminæ of mica partly imbedded. When heated very strongly it behaves like the former spars, and shows slight signs of fusion at a lower temperature. This mineral belongs to the group of difficultly fusible spars. Its analysis gave:—

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
64.08	21.73	0.93	0.53	0.78	1.48	10.08

= 99.61 per cent.

The chemical formula, $1 : 3.14 :: 10.31$, shows an increase of alumina. The second method of calculation gives $0.96(\text{Al}_2\text{O}_3, 3.37 \text{ SiO}_3) + \text{KO}$, or $0.96 \times 3.37 = 3.24$.

The second part of this paper describes further fusion experiments, undertaken with the view of confirming the author's supposition regarding the relation between pyrometric and analytical numbers. The following are the conclusions which he draws from his present investigations:

(1.) The law according to which a certain number calculated from the chemical composition may serve to indicate the fusibility of a felspar, has now been confirmed by the analysis of seven felspars from different localities, and its claim to generality is continually becoming more apparent. (2.) Felspars may be divided, according to their fusibility, into two groups, viz., less fusible or more acid felspars, with a relatively higher number, and difficultly fusible or less acid felspars with a relatively lower number. (3.) Modifications within the separate groups, especially if only slight, cannot be determined with sufficient accuracy by the fusibility number in accordance with the above law—

more especially in the group of difficultly fusible spars, whereas in the case of the more readily fusible spars, the pyrometric results so far as regards strict coincidence with the analytical numbers, leave nothing to be desired. D. B.

Devitrification of Vitreous Rocks. By S. MEUNIER (*Compt. rend.*, lxxxiii, 1083—1085).—The author here replies to some objections which Lévy has brought against the hypothesis of the production of crystalline rocks by devitrification of vitreous rocks. R. R.

Carbonic Acid Springs of the Kyll-Thal in the Eifel. (Preliminary Notice.) By H. VOHL (*Deut. Chem. Ges. Ber.*, ix, 1664—1666).—Many springs containing carbonic acid are found in the valley of the Kyll. They contain lithium, but are free from sulphuretted hydrogen. G. T. A.

Analysis of the Gases of the Grotta del Cane. By ET. FINOT (*Ann. Chim. Phys.* [5], ix, 135—136).—The following are the results of two analyses of the gases of this cavern:—

	I.	II.
Carbonic acid	25·38	25·69
Oxygen	18·46	20·13
Nitrogen	56·16	54·18
	100·00	100·00

If the carbonic acid be deducted it will be seen that the proportion of oxygen in the remainder is greater than that contained in atmospheric air. H. H. B. S.

Organic Chemistry.

Di-isobutylene. By A. BUTLEROW (*Deut. Chem. Ges. Ber.*, ix, 1687).—Schneider regards the condensation-products of the olefines as compounds of a peculiar constitution, but the author's researches have shown that this is not the case. Di-isobutylene combines with bromine and with hydriodic acid, yielding an octyl iodide, which was converted by moist silver oxide into the alcohol, boiling at 146·5—147·5°, smelling like pentamethylethol, and solidifying at -20° to white needles. The hydrocarbon and the alcohol are oxidised by chromic acid to common acetone and trimethylacetic acid, proving that di-isobutylene has the following structure, $(\text{CH}_3)_2\text{C}=\text{CH}.\text{C}(\text{CH}_3)_2$. At the same time an octoic acid is formed, which may be explained by assuming that during the oxidation some of the di-isobutylene first combines with water, which is then given off again, yielding the hydrocarbon $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \text{C} \text{---} \text{CH}_2.\text{C}(\text{CH}_3)_2$, which might form a primary alcohol.

C. S.

Action of Sodium Hydrate on Inactive Fermentation Amylic Alcohol. By S. BALBIANO (*Gazzetta chimica italiana*, vi, 402—406).—Chapman and Smith having stated that by repeated distillation from sodium hydrate, inactive amyl alcohol might be separated from the active fermentation alcohol, whilst Bakhoven said that by this method he had succeeded in obtaining a dextro-rotatory alcohol from the commercial alcohol, the author was induced to investigate the action of sodium hydrate both on pure inactive amylic alcohol and on commercial amylic alcohol. He found that the former was still inactive, even after thirty-two distillations from sodium hydrate, whilst twenty-three distillations from the hydrate sufficed to render commercial amylic alcohol completely inactive. No dextro-rotatory power could be observed even after forty-three distillations, so that, as Le Bel had previously found, Bakhoven's statements are incorrect. By these repeated distillations a small quantity of amyl oxide is formed, and a corresponding quantity of water eliminated. C. E. G.

Preparation of Ethyl Nitrate. By G. BERTONI (*Gazzetta chimica italiana*, vi, 406—407).—The author recommends the following modification of Lossen's process for preparing this ethereal salt. A mixture of 10 grams of urea and 150 cub. cent. of nitric acid, specific gravity 1.36, is heated in a retort until the nitrate of urea is dissolved, and white vapours begin to appear in the retort; 150 cub. cent. of alcohol of 92 per cent. are then added by means of a funnel reaching nearly to the bottom of the retort, the distillation being subsequently proceeded with until nearly the whole of the ethyl nitrate has passed over. Then 150 cub. cent. of acid, and an equal quantity of alcohol are added, the ethyl nitrate distilled off, and a similar operation performed four or five times, finally adding 50 cub. cent. of alcohol, and distilling. The amount of ethyl nitrate which passes over, mixed with water and some alcohol, is nearly that required by theory. C. E. G.

On the Rotatory Power of Mannite and its Derivatives. By G. BOUCHARDAT (*Compt. rend.*, lxxxiv, 34).—From former experiments, the results of which have been already published, it appears that mannite has a rotatory power, which is made evident by passing polarised light through a tube four meters long, containing a solution of that substance. This rotatory power is increased if the mannite exists as an ether, or if borax, sodium hydrate, or some other salts are present; mannite from various sources has the same rotatory power, and these rotatory powers are increased to the same degree by addition of borax, or by combination with nitric acid. The hexacetic and hexnitric ethers of mannite obtained from sugar have the same rotatory power as the derivatives of the mannite from the ash tree, and the hexacetic derivatives crystallise in the same form. These mannites are also identical with that obtained from β -glucose of milk sugar. The author contradicts Messrs. Müntz and Aubin, who assert that mannite has no rotatory power, and confirms the statement of Loir and Bichat, that mannite has a levo-rotatory power of $0^{\circ} 15'$, and in its behaviour with salts resembles narcotine, asparagine, amyl alcohol, &c. W. B.

Action of Heat on Quercite. By L. PRUNIER (*Compt. rend.*, lxxxiv, 184).—When quercite is dried at 100°, the proportion of carbon gradually increases from 43·7 per cent. to 45·01 per cent., obtained after four days' drying, while the hydrogen decreases from 7·5 to 7·3 per cent. These numbers correspond with a loss of H₂O in four molecules of quercite :



At temperatures above 100°, and at the ordinary pressure, quercite loses more water and melts at about 230°, producing a sublimate of crystals impregnated with a slightly coloured liquid. The non-volatile portion froths a great deal, and leaves a residue of charcoal.

When heated in an oil-bath under a pressure of about 2 cm. of mercury, it loses water and melts at 225°, and at about 235–240° it boils, the cool parts of the apparatus becoming covered with a sublimate of white needle-shaped crystals. No permanent gas is evolved even after six hours' heating, if the temperature be kept below 280°.

The fixed residue is transparent and nearly colourless, solidifying on cooling to an amorphous mass, having the appearance of gum-arabic; it is very deliquescent, and when dissolved in water and crystallised, furnishes quercite.

The crystalline sublimate gave on analysis 46·44 and 46·46 p.c. carbon, 7·50 and 7·80 hydrogen, leading to the formula C₁₂H₂₂O₉. Its formation from quercite is represented by the equation—



it is therefore the ether of quercite. It melts at 210°, is insoluble in alcohol and ether, and on long boiling with water, reproduces quercite. The gummy residue left in the retort gave 45·1 p.c. of carbon and 7·3 p.c. of hydrogen, that is the same numbers as quercite dried at 100°; it may be considered as a compound of quercite with quercitic ether. It is insoluble in alcohol and ether.

When the temperature is allowed to rise above 280° in a vacuum, the liquid froths and a distillate passes over, having a slightly acid reaction. At the same time carbonic acid is produced abundantly. At 310–315° a crystalline sublimate is produced, consisting of two kinds of crystals, one having the form of needles and the other that of rectangular plates. These bodies appear to be acids; one melts at 102°, the other at 110°; they are very soluble in alcohol.

If the non-volatile residue be treated with alcohol, a substance is extracted which, when strongly heated, gives a golden-yellow sublimate; and this on crystallising gives the well-known green compound of hydroquinone with quinone. Hydroquinone is, in fact, produced by the dehydration of quercite:



Effects of Heat on Cane-Sugar in Aqueous Solution. By L. LOUËD (*Bull. Soc. Chim.* [2], xxvi, 449).—The author has arrived at the following conclusions: Aqueous solutions of cane-sugar, heated to

100° in presence of air, yield inverted sugar; but when the solutions are heated out of contact with air, or in presence of air thoroughly purified, this transformation does not take place. Nitrogen and oxygen gases are without action, but carbonic acid produces the effect though more feebly than air. The transformation of the sugar is due, partly to the carbonic acid of the air, and partly to other substances in the atmosphere which have not yet been determined. R. R.

Researches on the Inversion of Sugar by Acids and Salts. By M. FLEURY (*J. Pharm. Chim.* [4], xxii, 423—424).—Having studied the inversion of sugar by different acids, using the latter in quantities proportional to their molecular weights, the author finds that there is no relation between the rapidity of inversion and the molecular weights of the bodies which produce it, but that, as far as his experiments went, hydrochloric acid seemed to act with the greatest energy. By using the same acid and varying proportions of sugar, it was found that the time required for complete inversion was constant, but when the quantity of acid varied, the duration of the operation was shortened as the weight of the latter was increased.

The action of acid sulphate of potassium and of aluminium sulphate upon sugar showed that these salts existed in the solution, in a state of partial decomposition; in the case of the latter salt the decomposition appeared to be progressive, but was not increased by the addition of acetic acid.

Solutions of ammonium sulphate and quinine sulphate were apparently without action upon sugar. J. W.

Researches on Melezitose. By A. VILLIERS (*Compt. rend.*, lxxxiv, 35).—The plant, *Alhagi Maurorum*, which exudes this manna, grows in Persia, and is used there as a purgative, under the name *Turanjbin*. After being boiled with animal charcoal, and evaporated to a syrup, it crystallised after some months in small brilliant crystals, which on recrystallisation from alcohol, formed large white crystals of the formula $C_{12}H_{22}O_{11} + H_2O$. It is dextrorotatory, its power being $+94^{\circ} 48'$, or for the sodium flame, $+88^{\circ} 51'$. On boiling with an acid, it is converted into glucose, and its rotatory power is reduced to that of glucose, viz., $+53$. It then reduces Fehling's solution. Nitric acid oxidises it to mucic and oxalic acids. Its melting-point is 140° . It is thus seen to be identical with Berthelot's melezitose. It crystallises in monoclinic (clinorhombic) prisms.

The mannite of alhagi also contains cane-sugar, which may be isolated by treating the mother-liquor of the melezitose with alcohol, and adding ether till a slight precipitate is formed. Crystals of cane-sugar are then deposited. The mother-liquor acts like a solution of cane-sugar containing dextrorotatory foreign substances, which are not fermentable with beer-yeast. W. R.

Remarks on the Preceding Paper. By BERTHELOT (*Compt. rend.*, lxxxiv, 38).—The occurrence of *melezitose* in the exudations of one of the Coniferae and in a leguminous plant, one found in France, and the other in Affghanistan, is interesting. *Trehalose* exists in

Echinops, and in cut rye, also in a number of mushrooms, and moulds. As cane-sugar is found together along with its isomeride melezitose, the mode of formation of the two sugars may be imagined. Cane-sugar, melitose, and milk-sugar, are formed by the union of two polyatomic alcohols, with elimination of water, and these two alcohols are different from each other. But melezitose and trehalose yield only one alcohol when decomposed, viz., grape-sugar (glucose). The two latter sugars may therefore be compared with ordinary ether; and if the glucose obtained from each of these two sugars is the same, it must be granted that two molecules of glucose may be united in two different ways, according to the molecule of water replaced. If glucose be viewed as at once a pentatomic alcohol and a monatomic aldehyde, three distinct isomeric types may theoretically result from the union of two molecules with elimination of water, viz. :—

1st. A *mixed ether*, the water being eliminated from two alcoholic groups, one in each of the molecules of glucose. The product would thus be a diatomic aldehyde, and an octatomic alcohol. A large number of isomerides is possible, depending on the primary, secondary, or tertiary nature of the alcohol groups affected.

2nd. A *mixed aldehyde*, a monatomic aldehyde like crotonic aldehyde, formed by the union of two molecules of a lower aldehyde, with elimination of water, and at the same time a decatomic alcohol.

3rd. An *ether-aldehyde*, the alcohol group of the one molecule of glucose combining with the aldehyde group of the other, water being eliminated. This body would be a monatomic aldehyde and a monatomic alcohol.

Of these three types, only the first and last can reproduce their constituents by assimilation of water.

This explanation would be sufficient were one of the constituent molecules of glucose transformable into ordinary glucose by the prolonged action of acids. But the author has not thought it necessary to theorise on the existence of isomeric saccharoses derived from the same glucose, and capable of reproducing them like trehalose and melezitose.

W. R.

Saccharine Matter contained in the Petals of Flowers. By J. BOUSSINGAULT (*Compt. rend.*, lxxxiii, 978—980).—The petals of the flowers were carefully separated, and the soluble matter extracted by a given volume of water; the non-saccharine matter was eliminated by the addition of basic acetate of lead. In the following table, column I gives the percentage of dry matter in the petals (the leaves of these plants were also examined); column II gives the percentage of sugar (in the petals in their natural state) capable of reducing copper solution; column III the percentage of invertible sugar, reducing the copper solution only after treatment with acid.

	I.	II.	III.
Lily petals	12.0	2.60	traces.
„ leaves	16.0	2.75	traces.
Oleander petals.....	16.0	7.22	traces.
„ leaves	26.5	2.46	traces.
Portulacca flowers.....	10.0	4.42	0.65
„ leaves	5.6	1.27	0.20
Acacia petals.....	13.0	3.80	0.00
Gum acacia petals	17.0	1.46	1.13
Rhododendron petals ..	8.0	2.20	0.50
Magnolia petals.....	11.5	1.44	0.55
„ leaves.....	24.0	1.34	0.76
Orange petals.....	21.0	5.00	0.60
„ whole flowers ..	22.0	4.11	0.94
„ leaves.....	28.0	traces.	1.30
Snap-dragon petals	14.0	4.83	2.12
Lime flowers	25.0	0.54	0.27
„ leaves	33.0	1.08	1.91
Rose petals.....	13.0	3.40	traces.

When exposed to the air after separation from the plant, the flowers lose their sugar, absorbing oxygen and exhaling carbonic anhydride, but this action takes place only while they are in their normal state, and ceases entirely when they are dried. F. D. B.

Differences in the Diastatic Reactions of Starch from different Sources. By A. DOBROSLAVINE (*Bull. Soc. Chim.* [2], xxvi, 452).—Starch from potatoes and from arrowroot required less saliva than the starch from wheat and from rice to produce the same quantities of glucose; and with the same quantity of saliva, starch from the former sources yielded more glucose than that from the latter, and in a shorter time. R. R.

Composition of Gun-Cotton. By F. A. ABEL (*Compt. rend.*, lxxxiii, 1011—1014).—Commercial gun-cotton is always a mixture of trinitrocellulose with the following substances in variable proportions.—(a.) Products of the action of the acids on fatty and resinous matters contained in the fibres of the cotton. (b.) Cellulose which has escaped the action of the nitric acid. (c.) Mineral substances. (d.) Nitrous products other than trinitrocellulose, and soluble in a mixture of alcohol and ether. The analyses of Ohampion and Pellet, having however given for a sample of compressed gun-cotton prepared by Abel's method, results which correspond with the formula of trinitrocellulose, the author points out that the accordance must be due merely to the proportion in which the other bodies accidentally happen to occur in the sample. R. K.

Action of Bromine on Acetone. By N. SALKOWSKY (*Deut. Chem. Ges. Ber.*, ix, 1687).—Monobromacetone is obtained by adding the required quantity of bromine to a solution of one part of acetone in 10 parts of water. It is a colourless, refractive liquid having a

very irritating smell; it is decomposed by heat, but may be distilled with steam; it forms a crystalline compound with acid sodium sulphite, and a crystalline but very unstable compound with dry ammonia, while aqueous ammonia converts it into basic compounds. Dibromacetone has a less pungent smell, and combines with acid sodium sulphite. On adding bromine to a well cooled aqueous solution of acetone, the compound $C_3H_5OBr_2$ is formed, which has previously been observed by Linnemann; it explodes when freed from water.

C. S.

Easy Method of Preparing Glycollic Acid. By C. Z. CROMMYDIS (*Bull. Soc. Chim.* [2], xxvii, 3—5).—On heating an aqueous solution of oxalic acid with granulated zinc at 100° for a week, filtering, and adding excess of lime, a solution is obtained containing calcium glycollate, with a little glyoxalate. The glycollate is easily obtained by removing the excess of lime by means of oxalic acid, boiling the liquid until the glyoxalate is destroyed, and concentrating by evaporation. The crystals which are deposited contain 5 mols. of water of crystallisation, one of which they lose on exposure to the air, and the other four at 100° , or over sulphuric acid *in vacuo*. The author also prepared the copper and zinc salts and the free acid.

C. E. G.

Diethyl-methyl-acetic Acid. By M. IDANOFF (*Bull. Soc. Chim.* [2], xxvi, 450).—Diethyl-methyl-acetic acid, $C(C_2H_5)_2(CH_3)CO_2H$, isomeric with *cananthic* acid obtained by the action of the iodonhydride of diethyl-methyl-carbinol on potassio-mercuric cyanide, HgK_2Cy_4 , and heating the cyanide produced with fuming hydrochloric acid in sealed tubes, boils at 207 — 208° , and is not solidified by a mixture of snow and salt. Its salts crystallise well.

R. R.

Modifications of Elæomargaric Acid produced by Light and Heat. By S. CLOËZ (*Compt. rend.*, lxxxiii, 943—945).—The oil obtained from the seed of *Elæococca vernicia*, when saponified with an alcoholic solution of potash, yields a well crystallised salt, from which may be separated a solid fatty acid melting at 48° . This is elæomargaric acid. Solutions of this substance in ether or carbon disulphide remain unchanged for an indefinite time when kept in the dark; but when they are exposed to light, the acid is modified, so that when the solvent is removed by distillation in a current of hydrogen, the residue melts at 71° . An alcoholic solution of the acid when exposed to light deposits fine crystals, which have the same composition as the original acid. This modification the author terms *elæostearic acid*.

When heated to 180° in sealed tubes containing hydrogen, these acids are changed into a liquid product having the same composition, but upon which light is without action. This modification receives the name of *elæoleic acid*.

F. D. B.

Cerotic Acid from Beeswax. By M. SCHALFRIEFF (*Bull. Soc. Chim.* [2], xxvi, 450).—The cerotic acid obtained from beeswax by Brodie's method has the composition $C_{27}H_{54}O_2$, and all the properties indicated by that chemist, but it is a mixture. The author has suc-

ceeded in separating several substances from it by fractional precipitation with lead acetate. Amongst others, he has obtained an acid which melts at 91° , and is approximately represented by the formula $C_{34}H_{68}O_2$. The same substance can also be separated from Brodie's acid by crystallisation from a solution in ether. R. R.

Action of Hydrocyanic Acid upon Pyruvic Acid. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, ix, 1621—1624).—This action results in the production of ordinary lactic acid. A calcium salt was also obtained, which appeared to contain both lactate and formate of this metal—



This reaction of pyruvic acid is explained by supposing that at first the acid is decomposed into aldehyde and carbon dioxide. The alde-

hyde combines with hydrocyanic acid to form $CH_3-\overset{\text{OH}}{\underset{\text{CN}}{\text{C}}}$ (1), from

which, by the action of hydrochloric acid, lactic acid is produced. The pyruvic acid then combines with hydrocyanic acid, forming $CH_3-\overset{\text{CN}}{\text{C}}-(\text{OH})-\text{COOH}$ (2). This substance loses CO_2 , and is re-

duced to (1) alone. If this explanation be the true one, pyruvic acid would appear to have the composition $CH_3-\text{CO}-\text{COOH}$.

M. M. P. M.

Electrolysis of Aqueous Solutions of Oxalic Acid. By N. BUNGE (*Bull. Soc. Chim.*, xxvi, 450—452).—The following are the author's results:—When aqueous solutions of oxalic acid are electrolysed, oxygen is disengaged at the positive pole, independently of carbonic acid. The volumes of the liberated gases have an exact ratio, since for each volume of hydrogen liberated at the negative pole half a volume of oxygen or two volumes of carbonic acid are set free at the positive pole. The relative quantity of carbonic acid contained in the gaseous products from the positive pole increases with the intensity of the current, other conditions remaining the same: it changes also with variations in the strength of the solution, the temperature, and the surface of the electrodes. R. R.

Action of Iodide of Allyl and Zinc on Ethyl Oxalate. By M. ZAYTZEFF (*Bull. Soc. Chim.* [2], xxvi, 454).—Among the products of the reaction the author found the ethylic ether of diallyloxalic

acid, $C_{10}H_{16}O_5$ $\begin{matrix} \text{O}(C_3H_5)_2\text{OH} \\ \text{CO.OC}_2\text{H}_5 \end{matrix}$, a colourless transparent liquid boiling at

213.6° . The author also separated diallyloxalic acid, which remains, after evaporation of its solution in ether, as an oily matter, which in dry air crystallises in feathery tufts. R. R.

Citric and Aconitic Acids. By P. HUNÄUS (*Deut. Chem. Ges. Ber.*, ix, 1749—1752).—Trimethyl citrate is formed by passing hydrochloric acid into a solution of citric acid in methyl alcohol. It forms well-defined triclinic crystals, melting at 78·5—79°, and boiling at 283—287°, with partial decomposition, into water and methyl aconitate. On boiling the ether with an insufficient quantity of potash, no salt of any of the acid ethers is formed, but some of the normal ether is completely decomposed. On heating the ether with acetyl chloride, it is converted into the liquid trimethylacetyl citrate, boiling at 280—282°. By the action of phosphorus pentachloride on trimethyl citrate, the trimethyl-ether of monochlorotricarballylic acid is formed, an oily liquid which is resolved by heat into hydrochloric acid and trimethyl aconitate, boiling at 270—271°. Experiments to prepare ethyl-citric acid were not successful. To prepare aconitic acid, citric acid is treated with hydrochloric acid at 140° for one day, the product dissolved in a little water, the solution evaporated, and the residue treated by Pawollek's method. C. S.

Observations respecting a Dextrogyrate Acid in Wine. By M. MAUMENÉ (*Journ. Pharm.* [4], xxii, 342).—Whenever sugar is oxidised very slowly, the first acid which is formed is *hexenic* acid, $C_6H_{14}O_7$ (mannitic); the second is *hexepic* acid, when the quantity of base present does not exceed one molecule for every molecule of sugar; with two molecules of base, *trigenic* is formed, and sometimes also *triachenic* acid.

Hexepic acid may be obtained in the pure state by the action of potassium permanganate on lactose; and trigenic acid (the gummic acid of Reichardt) appears also to be formed in the oxidation of glucose with alkaline copper solutions.

The object of the author in this communication appears to be to claim priority for the discovery of these acids in wine, since Béchamp in a previous note alludes to some new substance from a like source, which Maumené says presents some of the reactions of one or more of the acids above mentioned. J. W.

Potassium Cuprocyanide and Potassium Palladiocyanide. By M. VIDAÜ (*J. Pharm. Chim.* [4], xxii, 321—326).—The double cyanide of copper and potassium, $2KCy.CuCy_2$, may be prepared in solution by dissolving washed cupric hydrate in solution of potassium cyanide. By careful evaporation it separates in the form of colourless crystals having an alkaline reaction. This salt, as is generally known, answers to none of the ordinary tests for copper; it is not precipitated by a plate of iron, or by an alkaline sulphide or ferrocyanide, or by ammonia. These and similar reactions seem to show that in the salt in question the copper is intimately united with the cyanogen in a manner similar to that of iron in ferrocyanogen. In order, therefore to indicate this analogy, it is proposed to adopt the same nomenclature, and to name the salt *potassium cuprocyanide*.

The mineral acids and tartaric acid produce, in solutions of this salt, a white clotted precipitate, soluble in excess of the precipitant and in alkaline solutions. This precipitate, which is very unstable, is stated

to be cuprocyanic acid, H_2CuCy_4 , but no evidence is offered to show that it does not contain potassium, or that it does contain hydrogen. A solution of potassium cuprocyanide, like the ferrocyanide, gives an insoluble precipitate with most metallic salts. By dissolving cuprous hydrate instead of cupric hydrate in solution of potassium cyanide, a double cyanide results, which crystallises in light brown rhombohedral prisms, and behaves with reagents in a manner very similar to the salt previously described.

Potassium Palladiocyanide.—The double palladium salt is in every way strictly comparable with the corresponding copper compound. It is prepared in the same manner, is similar in appearance, and gives negative results with the ordinary precipitants of palladium, such as the alkaline sulphides and solution of potassium iodide. It does not precipitate salts of magnesium, aluminium, or ferric salts; it may therefore be used, if required, to separate the salts of magnesium from those of the alkaline earths, the salts of aluminium from zinc, and the ferrous from the ferric salts.

J. W.

Stains produced by Sulphocyanic Acid. By P. MIQUEL (*Bull. Soc. Chim.* [2], xxvi, 442—444).—The author remarks, that the red coloration acquired by animal and vegetable tissues under the influence of sulphocyanic acid is not a proof of the presence of ferric salts, since this reagent produces the red colour with a great number of other substances. A drop of sulphocyanic acid, placed on a sheet of paper free from iron, stains the paper of a deep red colour some distance around it by the spreading of the vapours. The colour disappears on exposure to the air, and its disappearance is hastened by a rise of temperature, or by a diminution of barometric pressure. Pure water also rapidly removes the colour; and similarly a solution of the acid does not deeply stain the paper until the water has nearly evaporated. Substances, free from iron, reddened by sulphocyanic acid, are acid, and become neutral only after the disappearance of the colour. Thus, ammoniacal vapours instantly remove the colour; hydrochloric acid restores it, and so on. Paper stained with sulphocyanic acid far surpasses red litmus in sensitiveness and sharpness for alkalis. Sulphocyanic acid is, therefore, not to be trusted in delicate researches, and the author recommends great caution in the use of alkaline sulphocyanates, inasmuch as they yield sulphocyanic acid in contact with bodies slightly acid.

R. R.

Asparagine and Aspartic Acid. By J. GUARISCHI (*Gazzetta chimica italiana*, vi, 370—391).—The author has already published a short account (*Gazzetta chimica italiana*, v, 245) of the action of urea on asparagine. When equal parts of the two substances are fused together, a beautifully-crystallised colourless compound is produced of formula $\text{C}_6\text{H}_7\text{N}_3\text{O}_3$; its composition and properties showing that it is the amide corresponding with uramidossuccinic anhydride, identical with the malilureic amide of Grimaux. Its formula the author believes to be $\text{CONH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}$. On boiling it with

hydrochloric acid, evaporating to dryness, and crystallizing the product from water, a substance is obtained in colourless prisms, only slightly soluble in cold water. Its solutions have an intensely acid reaction, and, on analysis, its composition was found to be $C_5H_5N_2O_4$, being that of *urimidosuccinic acid*, $COOH.CH_2.CH.NH.CO.NH$, the *malilureic acid*



of Grimaux. The *silver salt* of this acid $C_5H_4N_2O_4Ag_2$, is a white precipitate; the *barium salt* $(C_5H_3N_2O_4)_2Ba + 4H_2O$, crystallises in brilliant needle-shaped prisms, which lose their water of crystallisation at 120° .

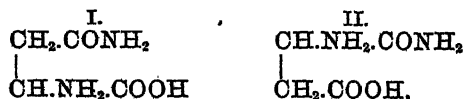
On heating a mixture of urea with twice its weight of aspartic acid at 130° for eight hours, ammonia was evolved, and the residue, on cooling, solidified to a friable mass. This, when treated with hydrochloric acid, evaporated to dryness at 100° , and crystallised from water, yielded urimidosuccinic or malilureic acid, identical with that previously mentioned.

The action of bromine on asparagine in presence of water is accompanied by the development of heat, and gives rise to tribromacetamide, $C_2H_2Br_3NO$, and dibromacetamide, $C_2H_2Br_2NO$, carbonic anhydride being evolved. Bromine does not appear to act on aspartic acid, at the ordinary temperature. Dibromacetamide melts at $156-157^\circ$. It crystallises from a concentrated solution in slender lustrous needles, which are only slightly soluble in ether or in cold water, but readily in alcohol. Tribromacetamide melts at $119.5-121^\circ$, and crystallises in colourless plates, which are soluble in cold water, and more soluble in alcohol than in ether. The author has also tried the action of nascent hydrogen, of phenol and of glycerin on asparagine, but as yet without any definite results.

After giving a summary of the various opinions as to the constitution of asparagine and aspartic acid, the author remarks that Kolbe's view, that the latter is amido-succinic acid $C_2H_5NH_2 \begin{array}{c} COOH \\ COOH \end{array}$ which may be written $CHNH_2.COOH$

$\begin{array}{c} | \\ CH_2.COOH. \end{array}$, is now almost invariably adopted.

For asparagine, however, two formulæ are possible, namely:—



The former of these (I.) appears preferable for various reasons, which the author discusses at length in five sections.

Determinations of the solubility of asparagine and aspartic acid at various temperatures were made, and it was found that the former requires 58 parts of water at 13° and 1.89 at 100° , whilst the latter requires 128 parts at 15° and 18.6 at 100° .

The action of hydrochloric acid, on aspartic acid, when the two are heated together in a water-bath and evaporated to dryness, appears to give rise to two products. These may be separated by heating the

dry residue in a current of carbonic anhydride at 120° for several hours, gradually raising the temperature to 200° , and then boiling repeatedly with water; the solutions thus obtained deposit a colourless substance on standing. This is readily soluble in ammonia or the alkalis, and yields a silver compound having the composition of *diargentate triaspartate*, $C_{15}H_{15}Ag_2N_3O_{10}$. The portion insoluble in water may be dissolved in ammonia, and gives a silver compound $C_6H_7AgN_2O_3$. C. E. G.

Condensation-products of the Ortho-homologues of Benzene. By B. REYMAN (*Bull. Soc. Chim.* [2], xxvi, 532—535).—The difficulties of preparing, in a state of purity and in sufficient quantity, the ortho-homologues of benzene were overcome by the adoption of the following process:—Bromine, suffered to fall drop by drop into cooled toluene, gives rise to brominated toluenes, which are dissolved in benzene. After the removal of the greater part of the solid compound by crystallisation, the solution is left for a week in contact with sodium. The oily matters are then separated by filtration, and the liquid is distilled. The portion passing over between 170° and 190° is again subjected to the same treatment of solution in benzene, addition of sodium, filtration and distillation, and this cycle of operations is several times repeated, until at length a product is obtained boiling at 180° , and this is nearly pure ortho-bromotoluene.

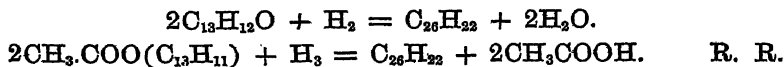
Orthoxylene was obtained by treating a solution of ortho-bromotoluene in benzene with methyl iodide and then with sodium, the vessels being kept cool. The filtered liquid, when subjected to fractional distillation, yielded a hydro-carbon, which was recognized as xylene. Orthoxylene, when treated with chlorine, deposited a carbonaceous matter, and yielded two well-defined chlorides of ortho-xylyl, a monochloride and a dichloride. R. R.

Action of Ammonia on Chloracetylbenzene. By W. STANDEL and L. RÜGHEIMER (*Deut. Chem. Ges. Ber.*, ix, 1758—1761).—When a solution of pure chloracetylbenzene is treated with ammonia-gas, and this treatment is repeated from time to time, two isomeric bodies $C_{16}H_{13}O_2Cl$ are formed. One is readily soluble in alcohol and ether, and crystallises in needles melting at 117° , while the second is much less soluble, and forms prisms melting at 154 — 155° . C. S.

Diphenylcarbinol and some of its Derivatives. By A. ZAGOUENNY (*Bull. Soc. Chim.* [2], xxvi, 452).—A mixture of three parts benzophenone and of one part caustic potash, dissolved in five parts of alcohol, was heated at 160° for five hours in a sealed tube. The product was treated with boiling water, to dissolve out excess of benzophenone, and the residue was diphenylcarbinol, melting at 68° , and very soluble in alcohol, ether, and acetic acid. This substance is also obtained by heating benzophenone, with a solution of alkali in amyl alcohol. The sealed tube is heated for five hours at 180° ; its contents remain clear, and the liquid contains, besides the diphenylcarbinol, valeric acid. Benzophenone, dissolved in an alcoholic solution of potash, and boiled for a long time with zinc, without contact of air,

is transformed into diphenylcarbinol. Benzophenone, dissolved in acetic acid and boiled with zinc, is converted into benzopinacone.

Diphenylcarbinol is not modified by the prolonged action of alcoholic potash in a sealed tube at 200°. Heated with sulphuric acid in a sealed tube at 180°, it yields the ether of diphenylcarbinol, a crystalline body fusing at 120°, and little soluble in boiling alcohol. Zinc is without action on an acetic acid solution of diphenylcarbinol in the cold; but, on boiling, an oily liquid collects on the surface, and on cooling forms a crystalline mass. This is tetraphenylethane, the formation of which may be thus explained:—



Action of dilute Sulphuric Acid on Hydrobenzoin and Isohydrobenzoin. By TH. ZINCKE (*Deut. Chem. Ges. Ber.*, 1769—1775).—By this action the two compounds yield a liquid and a solid product. The liquid obtained from both is the same; it is a colourless thick oil, which chromic acid resolves into benzophenone and carbon dioxide: it appears therefore to be the aldehyde of diphenylacetic acid, $(\text{C}_6\text{H}_5)_2\text{CH}.\text{COH}$.

The solid products are not identical; that obtained from hydrobenzoin crystallises from hot alcohol in glistening needles melting at 131—132°, and from ether in large rhombic crystals. The derivative of isohydrobenzoin separates from ether in large monoclinic crystals, melting at 100—101°. Both are isomeric with the liquid.

Chromic acid solution attacks both compounds but slowly, a little benzoic acid being formed; a solution of chromic trioxide in acetic acid acts more energetically, but only very small quantities of benzaldehyde and benzoic acid are obtained, the chief product consisting in both cases of crystalline neutral bodies, which appear to be identical.

From these results it appears that hydrobenzoin and isohydrobenzoin have the same constitution, and are, as well as their solid derivatives, physical isomerides.



Hydrobenzoin and isohydrobenzoin may be regarded as diphenylglycol, and their transformation into diphenylacetaldehyde is perfectly analogous to that of common glycol into aldehyde, and that of pinacone (tetramethylglycol) into pinacolin. C. S.

Researches on the Substituted Eugenols. By A. CAHOUS (*Compt. rend.*, lxxxiv, 151—157).—In a previous paper (*Ann. Chim. Phys.* [3], lii) the author has described a compound which he now calls ethyleugenol.

Eugenol being represented by the formula $\text{C}_6\text{H}_5 \left\{ \begin{array}{l} \text{OH} \\ \text{OCH}_3, \\ \text{C}_2\text{H}_5 \end{array} \right.$ which

would place it in the benzene series, ethylougenol would be represented by $C_6H_5 \begin{Bmatrix} OC_2H_5 \\ OCH_3 \\ C_3H_5 \end{Bmatrix}$, and the corresponding methyl-compound, the first term of the series, would have the formula $C_6H_5 \begin{Bmatrix} (OCH_3)_2 \\ C_3H_5 \end{Bmatrix}$.

By the gradual oxidation of these bodies, they can be transformed into compounds related to protocatechuic acid, in which two atoms of hydrogen are replaced by two atoms of methyl, or by one of methyl and one of ethyl, forming dimethyl- or methylethylprotocatechuic acids.

In order to obtain the eugenols resulting from the substitution of the homologues of ethyl for the hydrogen in normal eugenol, the iodides of the various radicles were heated with potassium-eugenol and a little alcohol in sealed tubes.

Propyleugenol, $C_{13}H_{18}O_2 = C_6H_5 \begin{Bmatrix} OCH_2CH_2CH_3 \\ OCH_3 \\ C_3H_5 \end{Bmatrix}$.—This compound

is obtained by heating in a flask, which is subsequently sealed in the blowpipe flame, a mixture of 100 parts of eugenol, 100 parts of propyl iodide, and 34 or 35 parts of potassium hydrate, previously dissolved in strong alcohol. The mixture, which must be shaken from time to time, deposits potassium iodide, after which the flask is heated for some hours in a water-bath, until the deposition of potassium iodide ceases, when the heat is withdrawn and the contents of the flask are treated with water; a heavy oil then separates, which is washed with potash and water, dried with calcium chloride, and finally distilled, the portion passing over between 260° and 270° being collected apart. This is pure propyleugenol.

Propyleugenol is a mobile liquid, of a light amber colour, with an odour resembling that of cloves. It is insoluble in water, but dissolves easily in alcohol and in ether. Its density is 1.0024 at 16° ; it boils between 263° and 265° . Bromine and fuming nitric acid attack it violently.

When suspended in about ten times its weight of hot water and shaken up with a hot dilute solution of potassium permanganate, added little by little, this substance is progressively oxidised, producing finally the potassium salt of an acid which can be isolated by concentrating the solution and saturating with hydrochloric acid. A deposit is thus obtained, which is hardly soluble in cold water. Hot water dissolves it easily and deposits it on cooling in silky needles. Alcohol dissolves it easily, and leaves it on spontaneous evaporation in fine yellowish prisms; ether also dissolves it. This product is the propylic derivative of methylprotocatechuic acid, $C_{11}H_{14}O_4 = C_7H_7(CH_3)(C_3H_7)O_4$.

Isopropyleugenol.—This compound is obtained by a process exactly similar to that employed in the preceding case. It boils between 252° and 254° , has a density of 0.199 at 17° , and is represented by the formula



By oxidation with potassium permanganate, it yields an acid which closely resembles that obtained from propyl-eugenol, and may be obtained in crystals by spontaneous evaporation of its alcoholic solution.

Butyleugenol, $C_{14}H_{20}O_2 = C_6H_5 \left\{ \begin{array}{l} OC_4H_9 \\ OCH_3 \\ C_3H_5 \end{array} \right.$ —This body is obtained in

the same way as the previous compounds, substituting butyl iodide for propyl iodide. It is a faint amber-coloured liquid, boiling between 272° and 274° , and having a density of 0.985 at 15° .

Potassium permanganate oxidises it, producing *methylbutylprotocatechuic acid*, $C_{12}H_{16}O_4 = C_7H_4(CH_3)(C_4H_9)O_4$.

Amyleugenol, $C_{15}H_{22}O_2 = C_6H_5 \left\{ \begin{array}{l} OC_5H_{11} \\ OCH_3 \\ C_3H_5 \end{array} \right.$ —This compound is pre-

pared in the same way as the preceding ones, and resembles them closely. It boils between 283° and 285° ; has a density of 0.976 at 16° , and is insoluble in water, but soluble in alcohol and ether. Its odour resembles, at the same time, that of cloves, and that of the amyl-compounds.

Potassium permanganate, at a temperature of $75-80^\circ$, oxidises it to *amylmethylprotocatechuic acid*, $C_{13}H_{18}O_4 = C_7H_4(CH_3)(C_5H_{11})O_4$.

Hexyleugenol.—This compound, obtained by the action of hexyl chloride on potassium-eugenol, is an amber-coloured liquid, boiling between 296° and 300° .

Allyleugenol.—This compound is obtained by the action of allyl bromide on potassium eugenol. On distilling the product, a portion passes over between 267° and 270° , then the temperature rises to 300° , and the liquid which then passes over solidifies on cooling into a resinous mass.

The first product gave figures leading to the formula $C_{13}H_{16}O_2$

$= C_6H_5 \left\{ \begin{array}{l} OC_3H_5 \\ OCH_3 \\ C_3H_5 \end{array} \right.$; it is, therefore, allyleugenol. The second body

gave the same figures, and is, therefore, a polymeride, boiling between 284° and 290° .

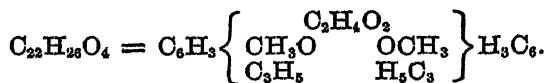
Benzyleugenol is prepared in the same way as the preceding compounds, and resembles them in every respect. It is partially decomposed by distillation.

Ethylene-eugenol.—Prepared by heating in a sealed tube, eugenol, alcoholic potash, and ethylene bromide. It is purified in the usual way, and then appears as a mass of splendid white plates, with nacreous reflections.

It is insoluble in water and cold alcohol, but dissolves in hot alcohol, which deposits it again on cooling in large nacreous plates, melting at 89° .

Ether, benzene, toluene, glacial acetic acid, and acetic ether dissolve it on heating, and deposit it on cooling in well-defined crystals. Nitric acid and bromine attack it violently.

Three analyses gave, as a mean, 74.58 per cent. carbon and 7.34 hydrogen, leading to the formula—



This compound is, therefore, derived from the union of two molecules of eugenol, in which the two atoms of basic hydrogen are replaced by the bivalent group, C_2H_4 , which serves to join them together.

Potassium permanganate oxidises this body, and transforms it into an acid insoluble in water, hardly soluble in alcohol and ether, which will be further examined. C. W. W.

Reactions of Aromatic Disulphides. By R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1637—1638).—Phenyl disulphide and boiling alcoholic potash act on each other as follows:—

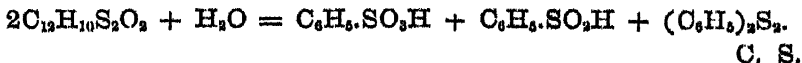


Tolyl disulphide acts in a similar way. Dry chlorine converts the disulphides into substitution-products of benzene, and in presence of water it forms sulphonie chlorides and acids. C. S.

Action of Sulphur Trioxide on Sulphydrates. By R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1638).—This reaction is expressed by the equation:



New Formations of Benzene- and Toluene-dioxydisulphide. By C. PAULY and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1639—1641).—These bodies are formed together with sulphonic acids when the sulphinic acids are boiled with water, or when their sodium salts are treated with sulphuric acid or phosphorus pentoxide. Pure benzene-disulphoxide, $\text{C}_{12}\text{H}_{10}\text{S}_2\text{O}_3$, forms transparent, monoclinic plates, melting at 45° . On boiling it with potash, it is decomposed as follows:—



Ethyl Benzenesulphonate. By R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1638—1639).—This compound is formed by the action of benzenesulphonic chloride on sodium ethylate. It is a heavy yellowish oil, having a faint vinous smell, and is decomposed by boiling water. C. S.

Constitution of Oxythymoquinone. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, ix, 1778—1781).—The author discusses his theoretical views and those of Gräbe and Ladenburg. C. S.

Tri-iodoresorcin. By A. MICHAEL and T. H. NORTON (*Deut. Chem. Ges. Ber.*, ix, 1752—1753).—When liquid iodine chloride is added, drop by drop, to a dilute aqueous solution of resorcin, tri-iodoresorcin, $\text{C}_6\text{H}_3\text{I}_3(\text{OH})_2$, is precipitated, crystallising from carbon

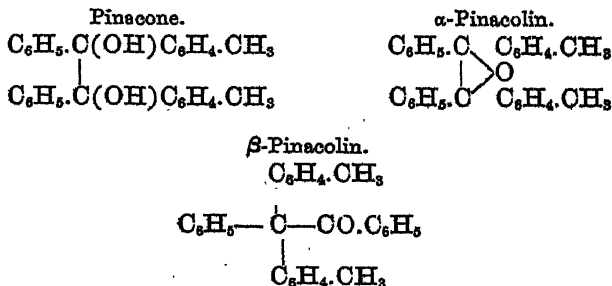
sulphide in long rose-coloured needles, melting at 145° , and subliming at 190° , with partial decomposition. It dissolves in carbon sulphide, alcohol, and ether, with a deep red colour, and in alkalis and aniline with decomposition, producing a brown solution. Boiling nitric acid converts it into styphnic acid. C. S.

Some Derivatives of Paratolylphenyl Ketone. By W. THÖRNER (*Deut. Chem. Ges. Ber.*, ix, 1738—1744).—When parabenzoylbenzenyl trichloride, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_3$, which is formed by the action of chlorine on the above ketone is treated with phosphorus pentachloride, the pentachlorinated ketone, $\text{C}_6\text{H}_5\cdot\text{CCl}_2\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_3$, is formed, crystallising from ether in thin rectangular glistening plates melting at $79\text{--}80^{\circ}$. On boiling it with an alkali, or treating it with nitric acid, it yields parabenzoylbenzoic acid.

By the action of zinc and hydrochloric acid on paratolylphenyl ketone two pinacolins are formed, which have already been described. The α -compound is much less stable than the β -pinacolin, and is easily converted into the latter by heating it with benzyl chloride on a water-bath, or with hydrochloric, hydriodic, or acetic acid to $150\text{--}160^{\circ}$.

Most oxidising agents do not act, or but slowly, on the pinacolins, but by adding a solution of chromic acid in acetic acid to a boiling solution of the α -compound in acetic acid, it is resolved into two molecules of the original ketone, while the β -pinacolin yields the acid, $\text{C}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{CH}_3)_2\text{CO}_2\text{H}$, which stands to the β -compound in the same relation as trimethyl-acetic acid to common pinacolin. This acid is almost insoluble in water, and separates from ether, &c., as a white amorphous powder. Its alkali-salts crystallise and are decomposed by carbon dioxide; the other salts are gelatinous precipitates.

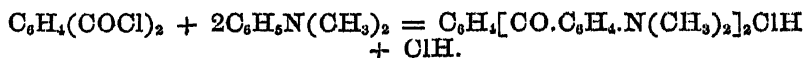
From these results it appears that by acting with zinc and hydrochloric acid on the ketone, first a pinacone is formed, which then, by loss of the elements of water, is converted into the instable α -pinacolin, and the latter by molecular change is transformed into the β -compound, which has a constitution analogous to the pinacolins of the fatty acids. The constitution of these compounds is therefore expressed by the following formulæ:—



When the latter compound is heated with hydriodic acid and amorphous phosphorus to $210\text{--}220^{\circ}$, it is converted into the hydrocarbon, $\text{C}_{22}\text{H}_{20}$, which is readily soluble in chloroform, carbon sulphide, and

toluene, and sparingly in hot alcohol and acetic acid, from which it separates in microscopic crystals melting at 213—213·5°. C. S.

The Phthaleins of Tertiary Aromatic Bases. By O. FISCHER (*Deut. Chem. Ges. Ber.*, ix, 1753—1757).—When phthalic chloride is added to dimethylaniline, a brisk reaction sets in, the mixture becomes first brown and on heating yellowish-green, when an effervescence takes place and the mass becomes dark green. The reaction must now be stopped by adding water; the product is then boiled to drive off the excess of dimethylaniline, and the remaining resinous mass purified by boiling it with ether, dissolving the residue in a little alcohol, and adding water, which precipitates the new compound. It is obtained pure by crystallisation from chloroform in green needles, having a yellowish-green reflection. This body is the monohydrochloride of dimethylaniline-phthalein, formed according to the equation—



On adding an alkali, the free base is obtained in greenish granules, which become white on filtration, but turn green again in the air.

The green monohydrochloride dissolves in concentrated hydrochloric acid with a yellowish-red colour, the dihydrochloride, $\text{C}_6\text{H}_4[\text{CO.C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{ClH}]_2$, being formed, which is obtained pure by passing hydrochloric acid gas into a dry ethereal solution of the base as a crystalline yellowish-red precipitate, which is very hygroscopic. When heated on the water-bath, it loses hydrochloric acid and is converted into the green salt. The two hydrochlorides combine with platinic chloride. $2\text{C}_6\text{H}_4[\text{CO.C}_6\text{H}_4(\text{NC}_2\text{H}_5)_2]_2\text{ClH} + \text{PtCl}_4$ is a bluish-green crystalline precipitate, which is formed by mixing alcoholic solutions of the two salts. $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2 \cdot 2\text{HCl} + \text{PtCl}_4$ is a crystalline yellowish-red precipitate, formed when a solution of the colour in concentrated hydrochloric acid is added to an alcoholic solution of platinic chloride. Both double salts are readily soluble in water. On mixing alcoholic solutions of the green salt and picric acid, a dark green precipitate of $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2 + \text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$ is obtained, while on adding a solution of the yellow salt to aqueous picric acid, a dark yellow precipitate is formed consisting of—



Dimethylaniline-phthalein combines, like phenol-phthalein, with nascent hydrogen. On adding zinc-dust to its acid solution, it soon becomes colourless, and soda then precipitates a colourless base, which forms a pale yellow picrate and an almost colourless platinic salt, having the composition—



Other tertiary aromatic bases form similar phthaleins.

C. S.

Action of Nitrils on the Haloid Ethers of Benzyl. By H. BRUNNER (*Deut. Chem. Ges. Ber.*, ix, 1744—1746).—The author's former experiments gave results similar to those lately published by Renesse. Silver nitrite and benzyl iodide yielded benzaldehyde and benzoic acid, while benzyl chloride yields an aromatic yellow oil, which contains nitrogen and is decomposed by heat. On heating potassium nitrite and benzyl chloride to 150°, the product consists of benzaldehyde, benzoic acid, anthracene, and liquid bodies containing nitrogen.

On heating benzyl chloride and silver nitrate, the nitric ether of benzyl is formed, which, on distillation, is decomposed, benzaldehyde and benzoic acid being formed. C. S.

Action of Hydriodic Acid on Naphthalene. By F. WREDEN and ZNATOWICH (*Bull. Soc. Chim* [2], xxvi, 449).—The action of hydriodic acid on naphthalene gives rise to a hexhydrocymene, $C_{10}H_{20}$, distilling between 155° and 160°, and to decahydronaphthalene, $C_{10}H_{18}$, boiling at 175—180°. Berthelot, who had studied this reaction, assigned to the first of these hydrocarbons the formula $C_{10}H_{22}$, and took the second for diethylbenzene, $C_{10}H_{14}$. R. R.

Derivatives of α - and β -Dinitronaphthalene. By A. ATTERBERG (*Deut. Chem. Ges. Ber.*, ix, 1730—1734).—The author has already shown that nitronaphthalene and α -dinitronaphthalene yield with phosphorus pentachloride, γ -dichloronaphthalene, melting at 107°; on nitration this body gives only nitro- γ -dichloronaphthalene, which phosphorus pentachloride converts into δ -trichloronaphthalene. Dinitro- γ -dichloronaphthalene crystallises from hot acetic acid in pale yellow, brittle, prismatic needles, melting at 246°. On treating it with tin and hydrochloric acid it is reduced to a *chloronaphthylamine*, which forms the *stannosochloride*, $C_{10}H_5Cl.NH_2.ClH + SnCl_2$, crystallising in large plates, which are sparingly soluble.

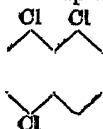
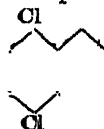
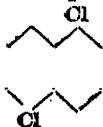
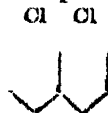
The *hydrochloride*, $C_{10}H_5Cl.NH_2.ClH + H_2O$, forms long prisms; on adding an excess of sulphuric acid to its solution and concentrating it, the *sulphate*, $C_{10}H_5Cl.NH_2.SO_4H_2$, is obtained in plates. Both salts are partially decomposed by boiling water, and give with ferric chloride first a greyish-green colour and then a precipitate.

ζ -Dichloronaphthalene is produced, together with δ -trichloronaphthalene, which forms by far the largest proportion of the product, by the action of phosphorus pentachloride on β -dinitronaphthalene; it forms rhombohedral crystals, melting at about 83°.

δ -Trichloronaphthalene is formed, not only by the action of chlorine or phosphorus pentachloride on β -dinitronaphthalene, but also from nitro- γ -dichloronaphthalene, α -dinitrochloronaphthalene, and monitro- β -dichloronaphthalene; but it is not easily obtained pure, as more highly chlorinated products are formed at the same time. It crystallises from hot alcohol and acetic acid in long, flat, soft needles, melting at 131°, and yields on oxidation a dichlorophthalic acid. C. S.

The Constitution of some Derivatives of Naphthalene. By A. ATTERBERG (*Deut. Chem. Ges. Ber.*, ix, 1734—1736).—The dif-

ferent modes of formation of δ -trichloronaphthalene described in the preceding paper, as well as the facts:—(1) That β -dichloronaphthalene is obtained from the nitronaphthol in which the two radicals are in the position $\alpha\alpha$; and (2) that γ -dichloronaphthalene can be prepared from α -nitronaphthalene and α -naphthalenesulphonic acid by converting them first into the nitrosulphonic acid, prove that the chlorine-atoms in δ -trichloronaphthalene are also in the α -position. Now as this compound yields α -dichlorophthalic acid and α -nitrophthalic acid, it follows that in γ - and ξ -dichloronaphthalene each aromatic group contains chlorine, and the constitution of these bodies is expressed by the following formulæ:—

 δ -Trichloronaphthalene. β -Dichloronaphthalene. γ -Dichloronaphthalene. ξ -Dichloronaphthalene.

But as these chloro-compounds are nearly connected with other di- and tri-substituted naphthalenes, the constitution of the latter is also known.

α -Monochloronaphthalene gives two dinitro-compounds, which, when treated with phosphorus pentachloride, both yield δ -trichloronaphthalene, showing that naphthalene must contain the α -position four times, which is a confirmation of Graebe's theory. C. S.

Dichlorinated Naphthalene analogous to Nitronaphthylsulphurous Acid. By P. Clève (*Bull. Soc. Chim.* [2], xxvi, 540).—The paper details the process by which, from the nitronaphthylsulphurous acid (already described by the author, p. 241), he obtained a compound in every way similar to the γ -dichlorinated naphthalene which Atterberg procured from nitro-compounds of naphthalene. R. R.

Phenolsulphuric Acids. By E. BAUMANN (*Deut. Chem. Ges. Ber.*, ix, 1715—1717).—These acids, which occur as normal constituents of the urine of mammals, are formed by boiling potassium pyrosulphate with an aqueous solution of a potassium phenate—



The potassium phenylsulphate thus obtained is identical with that obtained from human urine. By the same reaction the cresol isolated from horse's urine give the potassium salt of the same cresylsulphuric acid which occurs in that urine. C. S.

Paraxylenedicarbonic Acid. By L. KLIPPERT (*Deut. Chem. Ges. Ber.*, ix, 1766—1769).—When the dichloride $C_6H_4(CH_2Cl)_2$, obtained from paraxylene is boiled with potassium cyanide and alcohol, the nitril of paraxylenedicarbonic acid is formed, crystallising from ether, chloroform, or hot alcohol in glistening needles or plates, melting at 98° . It is easily decomposed by heating it with hydrochloric acid, and converted into paraxylenedicarbonic or paraxylenic acid, which is freely soluble in ether and alcohol, moderately soluble in hot water, and crystallises in flat silky needles melting at 244° . $C_6H_4(CH_2CO_2)_2Ba + 2\frac{1}{2}H_2O$ forms transparent needles; the calcium salt crystallises on evaporation in thin plates, with 2 mol. of water, and by precipitating its solution with alcohol in needles with 3 mols. of water. The anhydrous copper salt is a green crystalline precipitate, the zinc salt is amorphous, and the silver salt a white crystalline powder. The methylic ether, $C_6H_4(CH_2CO_2CH_3)_2$, crystallises in pearly plates, melting at 56.5 — 57° , and the ethyl-ether is a similar body, which melts at 57.5 — 58° . The chloride is an oily liquid which is decomposed by heat. The *amide* separates as a crystalline powder when the nitril is boiled with alcoholic potash; it is sparingly soluble in most solvents, and melts at 290° . When a solution of the cyanide in alcoholic ammonia is saturated with hydrogen sulphide, and allowed to stand, or heated to 100° , *paraxylenic sulphamide*, $C_6H_4(CH_2CS.NH_2)_2$, separates out in hard, yellow, crystalline crusts, melting with decomposition at 205 — 206° . C. S.

Action of Zinc-dust on the Chlorides of Sulphoparabromobenzoic Acid. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, ix, 1782—1787).—The crude chloride contains another body which seems to be an isomeride. By acting on the mixture with zinc-dust, the following compounds were obtained.

Sulphiparabromobenzoic acid, $C_6H_3Br(SO_2H)CO_2H$, crystallises from water in very brittle needles. The anhydrous normal barium salt forms small needles, and the acid salt long needles containing 2 mols. of water. The normal calcium salt is very freely soluble in water and alcohol; $[C_6H_3Br(CO_2H)SO_2]_2Ca + 8H_2O$ crystallises in long needles.

Bromobenzaldehydesulphinic acid, $C_6H_3Br(COH)SO_2H$, crystallises in long, pointed, broad prisms, melting at 131° . $(C_6H_3Br(COH)SO_2)_2Ba + 5H_2O$ forms large transparent prisms, which soon crumble down into a crystalline powder, without loss of water; on scratching them this takes place at once.

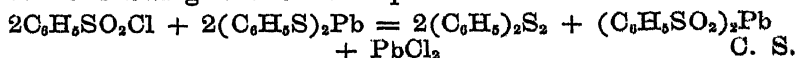
Hydrosulphobromobenzaldehyde and *Hydrosulphobromobenzoic acid* are most difficult to separate. A mixture of these substances has already been described (this volume, p. 413). C. S.

Phenyl Thiobenzoate and Paratolyl Thiobenzoate. By R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1634—1636).—The phenyl-ether is obtained by heating phenyl sulphhydrate with benzoyl chloride. It crystallises from hot alcohol or benzene in long glistening needles, melting at 56° . On acting on it with chlorine in the presence of water, it yields benzoic acid and benzenesulphonic chloride and acid.

The tolyl-compound is obtained by an analogous reaction, and crystallises from alcohol in large transparent prisms, melting at 75° .

C. S.

Experiments for Preparing the Thio-ethers of Benzenesulphonic and Paratoluenesulphonic Acids. By R. SCHILLER and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1636—1637).—These compounds are not obtained by the action of aromatic sulphhydrates on sulphonic acids or chlorides, whereas, on using the lead-salts of the sulphhydrates the following reaction takes place:—



C. S.

Benzylisoxylene and Benzoylisophthalic Acid. By A. BLATZBECKER (*Deut. Chem. Ges. Ber.*, ix, 1761—1766).—The benzylisoxylene which was used for these experiments was obtained from commercial xylene, and therefore probably a mixture of the meta- and para-compound. It is a colourless liquid boiling at 283° , and having a faint aromatic smell. On oxidising it with chromic acid solution, it yields benzylisophthalic acid, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, which is sparingly soluble in water, chloroform, and toluene, but freely in alcohol and ether. On adding water to its alcoholic solution, it separates out in crystalline crusts melting at 278 — 280° . The potassium salt is readily soluble, and crystallises in square plates. $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4(\text{CO}_2)_2\text{Ba} + \text{H}_2\text{O}$ separates in glistening needles when alcohol is added to its aqueous solution.

$\text{C}_6\text{H}_5\text{CO}\cdot\text{C}_6\text{H}_3(\text{CO}_2)_2\text{Ca} + \text{H}_2\text{O}$ forms needles or plates, and the anhydrous insoluble silver salt is a white powder. By acting on it with ethyl iodide, the ethyl-ether is obtained crystallising in needles melting at 94° ; the methyl-ether is a similar body melting at 117 — 118° .

When the acid is treated with zinc and hydrochloric acid, it is converted into benzhydrylisophthalic acid, which, however, like the acids of a similar constitution, is very unstable, and at once changes into the

anhydride, $\text{C}_6\text{H}_5\cdot\text{CH} \begin{array}{c} \diagup \text{C}_6\text{H}_5 \diagdown \\ \diagdown \text{CO}_2\text{H} \diagup \\ \diagup \text{CO} \diagdown \\ \diagdown \text{O} \diagup \end{array}$, which crystallises from alcohol in

needles melting at 206 — 207° . $(\text{C}_{15}\text{H}_9\text{O}_4)_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$ crystallises from hot water in glistening needles. $\text{C}_{15}\text{H}_9\text{O}_4\cdot\text{C}_2\text{H}_5$ forms plates or prisms, melting at 114 — 115° .

When this anhydride, or benzoylisophthalic acid, is reduced by sodium-amalgam, benzylisophthalic acid, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, is formed, crystallising in small needles melting at 242 — 243° . $\text{C}_{15}\text{H}_{10}\text{O}_4\text{Ba}$ is less soluble in hot than in cold water, and forms a crystalline powder. $\text{C}_{15}\text{H}_{10}\text{O}_4(\text{C}_2\text{H}_5)_2$ is a thick, oily liquid.

C. S.

Nitro- and Amido- Naphthylsulphurous Acids and their Derivatives. By P. T. CLEVE (*Bull. Soc. Chim.* [2], xxvi, 444—448).—By the action of nitric acid on the lead salt of β -naphthylsulphurous acid, two isomeric nitro-acids are formed. These may be separated by the different solubility of their barium salts in boiling water. The acid of the more soluble salt the author terms the δ -acid, and that of

the less soluble salt the β -acid. It is the latter which is described in the paper. The free acid is very soluble, and crystallises in yellow radiating needles. It is soluble in alcohol, has a bitter taste and forms soluble yellow salts. The paper describes the properties, and gives the analytical figures for a number of the salts, from which it appears that these have the formula $C_{10}H_8(NO_2)SO_3M'$. Phosphorus perchloride readily acts on the potassium salt, forming a chloride by replacing OK by Cl. By the action of ammonia on the chloride, the latter is converted into an amide, $C_{10}H_8(NO_2)SO_2NH_2$.

β -Nitronaphthylsulphurous acid is easily reduced by ammonium sulphide, and when excess of hydrochloric acid is added to the solution, a precipitate is obtained of amido- β -naphthylsulphurous acid, which is purified by solution in sodium carbonate, and reprecipitation by hydrochloric acid. It crystallises in the anhydrous state in thin rhombic plates, or with $2H_2O$ in slender flexible needles. Its colour is yellowish, but when exposed to the air this changes to violet-red. It forms soluble, crystallisable salts of a yellow colour, several of which are described in the paper. The solutions become deeply coloured when exposed to the air. The formula of the salts is $C_{10}H_8(NH_2)SO_3M'$.

R. R.

Methyl Santonate. By S. CANNIZZARO (*Gazzetta chimica italiana*, vi, 355—356).—To prepare this compound a solution of 1 mol. of santonic acid, $C_{15}H_{20}O_4$, and 4 mols. of potassium hydrate, $4KHO$, are dissolved in methyl alcohol and the solution is evaporated to dryness. The residue is then heated with methyl alcohol and excess of methyl iodide under a pressure of two atmospheres. During the reaction much methyl oxide is evolved. The methyl santonate may also be formed by the action of methyl iodide on a solution of sodium santonate in methyl alcohol. After distilling off the unattacked methyl iodide and part of the alcohol, water is added, and the methyl santonate extracted by agitation with ether. The oily residue left on evaporating the ethereal solution is washed with water, and a solution of acid sodium sulphite, and finally purified by crystallisation from ether and from methyl alcohol. *Methyl santonate*, $C_{15}H_{18}O_4 \cdot CH_3$, crystallises in colourless needles, which melt at $86-86.5^\circ$.

C. E. G.

Derivatives of Santonic Acid. By S. CANNIZZARO (*Gazzetta chimica italiana*, vi, 341—348).—*Hydrosantonic acid*, $C_{15}H_{22}O_4$, the sodium salt of which is obtained in micaceous laminae by treating a solution of sodium santonate with sodium-amalgam of 5 per cent., is thrown down on the addition of hydrochloric acid to a solution of the sodium-compound. It separates from its ethereal solution in colourless crystals belonging to the trimetric system. It melts and decomposes at 170° , is less soluble in alcohol and in ether than santonic acid, and is dextrorotatory. *Sodium hydrosantonate*, $C_{15}H_{21}NaO_4 \cdot 3H_2O$, crystallises in the trimetric system; exposed to the air it loses part of its water of crystallisation. The crystals of *potassium hydrosantonate* have the composition $C_{15}H_{21}KO_4 \cdot 2H_2O$.

Acetylhydrosantonide, $C_{17}H_{22}O_4$, is a substance crystallising in colour-

less needles, obtained by acting on hydrosantonin acid with acetyl chloride in excess—



It melts at 204° , and sublimes at a higher temperature. It is but little soluble in ether, and almost insoluble in water. It is not decomposed by a hot solution of potassium hydrate, but when heated with alcoholic ammonia at 130° , it yields a substance having the composition of hydrosantoninamide. *Benzoylhydrosantoninide*, $\text{C}_{22}\text{H}_{24}\text{O}_4$, prepared in a similar manner, also crystallises in colourless needles. It melts at 157° . It closely resembles the acetyl compound, but is decomposed when heated with a solution of potassium hydrate.

Hydrosantoninamide (?) $\text{C}_{16}\text{H}_{23}\text{NO}_3$, is formed on heating acetyl- or benzoyl-santonin with alcoholic ammonia at 120 – 130° . The product is evaporated, and then, after being washed with ether to remove the acetamide and benzamide simultaneously produced, is crystallised from alcohol. It melts at 190° , but with decomposition. It is soluble in alcohol, less so in ether, and only slightly in boiling water.

Metasantonin acid, $\text{C}_{15}\text{H}_{20}\text{O}_4$, is isomeric with santonin acid, and like it, monobasic. On adding argentic nitrate to a solution of sodium hydrosantoninate, a white precipitate of silver hydrosantoninate is produced, which dissolves on heating the liquid, metallic silver being deposited. On continuing to heat for about an hour, adding sodium hydrate from time to time so as to keep the solution nearly neutral, and finally precipitating the silver oxide remaining in solution by excess of the alkali, a liquid is obtained which, when filtered and acidified with nitric acid, deposits metasantonin acid in the crystalline state. A further quantity may be obtained from the solution, by agitating it with ether. When purified by repeated crystallisation from ether, it melts with decomposition at 161 – 167° . The alkaline salts of this acid are very soluble. The author has compared the rotatory power of solutions of santonin and metasantonin acids in various solvents, using Cornu's apparatus, and finds that the specific rotatory power of the latter acid is always greater than that of the former.

O. B. G.

Photosantonin Acid. By F. SESTINI (*Gazzetta chimica italiana*, vi, 357–369).—As far back as 1865 (*Repertorio ital. chim. pharm.*, 1865) the author observed that when an alcoholic solution of santonin was exposed to direct sunlight, it was decomposed, with production of an amorphous resinous substance, a small quantity of formic acid, and a crystalline compound which the author has since ascertained to be the diethylic salt of photosantonin acid, $\text{C}_{15}\text{H}_{18}(\text{C}_2\text{H}_5)_2\text{O}_4$, an acid isomeric with santonin acid. In this reaction if the alcohol is anhydrous, nothing but amorphous resinous compounds are obtained, whilst with aqueous alcohol, ethyl photosantonate is produced with but comparatively little resin, 85 grams of santonin in 6 litres of alcohol of 65 per cent. having yielded 28 grams of the ether after being exposed to the summer sun for a month. On substituting methyl for ethyl alcohol, the corresponding methyl compound is produced. The ether is pre-

precipitated in the crystalline state on mixing the alcoholic solution with 6 to 8 times its volume of a dilute solution of sodium carbonate, and may be purified by crystallising it first from alcohol, and then from ether-alcohol. Photosantonin acid is also formed when an aqueous solution of sodium santonate, or santonin, suspended in a solution of sodium carbonate, is exposed to sunshine. A similar transformation is effected by the insolation of a solution of santonin in glacial acetic acid of 95 per cent.; this being, in fact, the most convenient method of obtaining free photosantonin acid. The free acid may also be obtained from the ether by saponification with a dilute solution of sodium hydrate, or with baryta-water. *Photosantonin acid*, $C_{15}H_{13}O_4 \cdot H_2O$, crystallises from its alcoholic solution in colourless prisms belonging to the trimetric system. It is only slightly soluble in boiling water, but readily in alcohol, ether, and chloroform. It loses its water of crystallisation at 100° , and then melts at 153° .

Photosantonin acid decomposes the alkaline carbonates, with the aid of heat, but does not yield crystalline compounds. *Calcium photosantonate*, $(C_{15}H_{13}O_4)_2Ca + 4H_2O$, crystallises in white silky needles, soluble with difficulty in cold water. On heating this salt with calcium hydrate, a dicalcic salt is obtained which is readily soluble in water, but may be precipitated in white amorphous flocks by addition of alcohol. *Barium photosantonate*, $C_{15}H_{13}BaO_4 + 2H_2O$, is a white amorphous substance precipitated by alcohol from its aqueous solution.

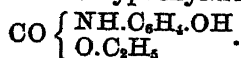
Silver photosantonate, $C_{15}H_{13}Ag_2O_4 + 4H_2O$, is obtained as a white precipitate on adding silver nitrate to a solution of barium photosantonate. The *Diethyl photosantonate*, obtained in the manner previously mentioned by exposing a solution of santonin in dilute alcohol to direct sunlight, is identical with that prepared synthetically by the action of ethyl iodide on silver photosantonate. It crystallises in large very thin plates, which melt at $67-68^\circ$. It is noteworthy that both this compound and ethyl santonate become liquid in contact with moderately dilute nitric acid. *Methyl photosantonate*, prepared by the insolation of santonin dissolved in methyl alcohol, crystallises in long prisms, which melt at 56.5° , and are readily soluble in alcohol or ether, and but little soluble in water. The methyl compound prepared synthetically from methyl iodide and silver photosantonate, melts at $51-52^\circ$.

C. E. G.

The Crystalline Form of some Derivatives of Santonin. By G. STRUEVER (*Gazzetta chimica italiana*, vi, 349-355).—This paper contains crystallographic measurements of santonic acid, metasantonin acid, hydrosantonin acid, photosantonin hydrate, sodium santonate, sodium hydrosantonate, and potassium hydrosantonate.

C. E. G.

The Action of Chloro-carbonic Ether on Amidophenol. By E. GRENVIE (*Bull. Soc. Chim.* [2], xxv, 177-180).—The action of chlorocarbonic ether on a solution of the amidophenol from volatile nitrophenol in ether yields metaoxyphenylurethane,



The crude product left on evaporating the ether is washed with hydrochloric acid and recrystallised from a mixture of alcohol and ether. The pure substance melts at 85°, and crystallises in tabular prisms; it is nearly insoluble in cold water, and but slightly soluble in boiling water or in hydrochloric acid, but is easily dissolved by solutions of potash, soda, or ammonia.

Heated to 200° it breaks up into alcohol and a body which the author calls oxycarbanil, thus—



Oxycarbanil is easily soluble in alcohol and alkaline solutions; it crystallises from boiling water in needles melting at 136°. The ammoniacal solution leaves the body unaltered on evaporation, and when heated to 160° in sealed tubes it forms amidophenol. Dry ammonia gas is also without action on the body.

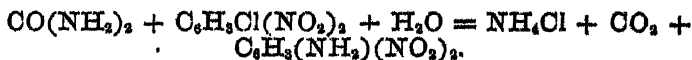
Orthoxyphenylurethane is formed by the action of chlorocarbonic ether on orthamidophenol (from nitrophenol, m.p. 110°). This body is very soluble in alkaline solutions, and crystallises in tabular crystals belonging to the clinorhombic system, which melt at 120°. The solution in potash blackens on boiling, and liberates alcohol. On dry distillation the body is decomposed.

W. H. P.

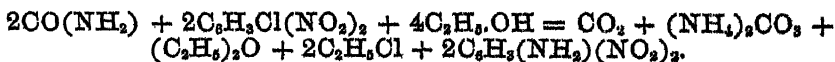
Action of α -Dinitrochlorobenzene on Acetamide. By WILLGERODT (*Deut. Chem. Ges. Ber.*, ix, 1717).—On heating equivalent quantities of these bodies with alcohol of 90 per cent. for some time to 150°, no reaction takes place, while on adding *magnesia usta* the decomposition is very incomplete, a little dinitraniline, magnesium chloride, and acetic ether being formed.

C. S.

Action of α -Dinitrochlorobenzene on Carbamide. By WILLGERODT (*Deut. Chem. Ges. Ber.*, ix, 1718—1722).—When these bodies are heated with strong alcohol to 150°, hardly any action takes place, while on using dilute alcohol or water the following reaction takes place:—



On using absolute alcohol, the action takes place only at 200—230°:—



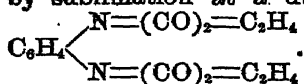
Dinitraniline is also formed if the two bodies are heated together without the addition of water or alcohol.

C. S.

Chlorinated Anilines. By F. BEILSTEIN and A. KURBATOW (*Deut. Chem. Ges. Ber.*, ix, 1688).—When metachloraniline is chlorinated, it yields orthodichloraniline melting at 71·5°, paradichloraniline melting at 50°, and two trichloranilines. One of the latter,

which melts at 95°, is identical with that formed by the reduction of the nitrotrichlorobenzene melting at 58°; the second melts at 67·5°, and yields an acetyl-compound melting at 120—122°; and by the diazo-reaction the trichlorobenzene melting at 53—54° and boiling at 218—219°. The nitro-compound of the latter, melting at 55—56°, gives with alcoholic ammonia a dichloronitraniline which melts at 162—163°, and which by the diazo-reaction is converted into ortho-dichloronitrobenzene melting at 43°. When the trichloraniline melting at 67·5° is converted into the diazo-platinum salt, and this is heated with soda, the tetrachlorobenzene melting at 45° and boiling at 254° is obtained. C. S.

Disuccinylphenylenediamine. By R. BIEDERMANN (*Deut. Chem. Ges. Ber.*, ix, 1668—1670).—Phenylenediamine and succinic acid were kept at a temperature of 200° for half an hour. After boiling with hot water, a crystalline body was obtained which perfectly resisted all ordinary solvents. Glacial acetic acid dissolves a small quantity of it, and by this means brilliant crystals may be formed. This body melts at a high temperature, above the limits of the mercurial thermometer. It can be obtained in brilliant white needles by sublimation at a dull red heat. The formula of the body is



It combines neither with bases nor with acids; but on long-continued boiling with alkalis, splits up into phenylenediamine and succinic acid. It withstands the action of fuming nitric acid, but dissolves in this acid in considerable quantity when heated, and is precipitated unchanged on cooling. A mixture of concentrated sulphuric and the strongest nitric acid, or of phosphoric anhydride and nitric acid, produces a yellow nitro-substitution compound.

Phthalic anhydride forms compounds, as succinic acid does, with the diamines. The author has prepared compounds by melting phthalic anhydride with meta- and para-phenylenediamine, and also with tolylenediamine (melting point 99°). Oxy-acids, such as the salicylic, also appear to yield similar condensation-products.

G. T. A.

New Researches on Diazo-compounds. Constitution of Compounds of Diazobenzoic Acid. By GRIESS (*Deut. Chem. Ges. Ber.*, ix, 1653—1660).—The compound $\text{C}_7\text{H}_5\text{N}_2\text{O}_5$ is, according to Kekulé, comparable to the haloïd compounds of organic radicles, and has the formula $\text{C}_7\text{H}_5\text{N}_2\text{O}_2\cdot\text{NO}_3$, while, according to Griess, it is a nitrate-diazobenzoic acid, $\text{C}_7\text{H}_4\text{N}_2\text{O}_2\cdot\text{HNO}_3$. So also the compound $\text{C}_7\text{H}_4\text{N}_2\text{O}_2\text{Br}$ is written by Kekulé $\text{C}_7\text{H}_5\text{N}_2\text{O}_2\cdot\text{Br}$, and by Griess $\text{C}_7\text{H}_4\text{N}_2\text{O}_2\cdot\text{HBr}$.

Nitrate-orthodiazobenzoic acid is prepared by passing nitrous acid into a mixture of nitrat-ortho-amidobenzoic acid (anthranilic acid) with nitric acid diluted with an equal volume of water at freezing temperature, till perfect solution takes place, and the nitrous acid is in excess. The solution is mixed with strong alcohol and ether, and the

compound is thrown down in almost white rhombic or six-sided plates or prisms, which are easily soluble in cold water, but not so readily in alcohol, and explode when heated. On boiling the aqueous solution, salicylic acid, nitrogen, and nitric acid are formed.

Hemi-nitratorthodiazobenzoic acid is formed from the above compound by dissolving it in a little cold water, mixing the solution with alcohol and ether, and repeating the operation with the crystals which are deposited. It consists of long white needles, and closely resembles the foregoing compound, especially in its decomposition by boiling with water. It is identical with the body described some years ago by the author under the name of diazo-salicyl nitric acid. The formula of this body is $2(C_7H_4N_2O_2)HNO_3$. It could not exist if Kekulé's hypothesis were correct.

Sulphato-metadiazobenzoic acid, $C_7H_4N_2O_2.H_2SO_4$, is formed by passing nitrous acid into a mixture of sulphatamidobenzoic acid with nitric acid. The nitratometadiazobenzoic acid is filtered off, and the filtrate is mixed with alcohol and ether; when almost white long laminae are deposited, which are extraordinarily soluble in water and explode when heated.

Two-fifths-sulphato-metadiazobenzoic acid, $5(C_7H_4N_2O_2).2H_2SO_4$, is formed by dissolving the last salt in the least possible quantity of water, mixing with alcohol and ether, and treating the crystals which separate out about five times in the same way. It consists of small acicular crystals which decompose on boiling, with formation of oxybenzoic acid, nitrogen, and sulphuric acid.

The rational constitution of nitrate-metadiazobenzoic acid is probably $C_6H_3=N_2.HNO_3$
CO.OH

Hydrodiazobenzoic acid, $C_7H_5N_2O_2$.—One part of nitrate-metadiazobenzoic acid mixed with water is gradually added to two parts of a cold concentrated solution of neutral potassium sulphite, the mixture warmed and then treated with excess of hydrochloric acid. On cooling, crystals of potassium diazobenzosulphonate are deposited. If this salt is acted on by tin and hydrochloric acid, and, after removal of the tin by sulphuretted hydrogen, is evaporated down till crystallisation begins, then saturated with ammonia, and afterwards with acetic acid, hydrodiazobenzoic acid separates on cooling in brownish crystals. When purified, the crystals consist of either yellowish, thin, and elliptic, or of badly formed 3–6-sided laminae. The acid has neither taste nor smell, and melts with decomposition at 186° . It is soluble with difficulty even in hot water, and also in alcohol, insoluble in ether. It shows a strongly acid reaction towards vegetable colours.

Hydrochloride of hydrodiazobenzoic acid, $C_7H_5N_2O_2.HCl$, is soluble with difficulty in cold, easily in hot water. If the aqueous solution is mixed with hydrochloric acid, it separates out in white needles or in long small laminae.

Barium hydrodiazobenzoate, $(C_7H_5N_2O_2)_2Ba + 4H_2O$, is formed by dissolving barium carbonate in a hot aqueous solution of hydrodiazobenzoic acid, and crystallises in small warty masses easily soluble in water.

Hydrodiazobenzoic acid exactly agrees in its reactions with Fischer's phenylhydrazin, except that by treatment with nitrous acid it directly forms an imide. Diazobenzene nitrate forms with hydrodiazobenzoic acid the imides of diazobenzoic acid and diazobenzene, together with aniline and amidobenzoic acid, and the same bodies are produced by the action of nitrate-diazobenzoic acid on hydrodiazobenzene (phenylhydrazin). In both cases a double compound, $C_{13}H_{12}N_4O_2$, is probably first formed.

Hydrodiazobenzoic acid may also be made by treating potassium diazobenzosulphonate with zinc and acetic acid. Potassium hydrodiazobenzosulphonate, $C_7H_4N_2.H_2.SHKO_3$, is formed in solution, and may be crystallised out after removal of the zinc. When this salt is boiled with hydrochloric acid it splits up into hydrodiazobenzoic acid and sulphuric acid. If, on the contrary, it is boiled with caustic potash, benzoic acid, nitrogen, and sulphurous acid are formed.

G. T. A.

Taxine, a Poisonous Alkaloid present in the Leaves and Seeds of *Taxus baccata* (L.). By W. MAVINÉ (*Chem Centr.*, 1876, 166—167).—Although cases of poisoning by yew-berries have been confirmed in former times and also recently, the poisonous effects of the fruits and seeds of the yew-tree are disputed from many sides, while the strongly toxic action of the other portions of the tree are known generally.

Lucas isolated from the leaves of this tree three grains of a body which he calls taxine, and gave a few reactions regarding it. For its preparation Stass's method for detecting alkaloids was followed out, without giving satisfactory results. The following process was more successful:—The leaves or seeds are powdered, and repeatedly exhausted with ether; the extracts are mixed, and the ether is distilled off. The residue which when obtained from the leaves, forms a green resinous mass, having a peculiar aromatic smell and sharp taste, while that from the seeds is a large quantity of a fatty oil, was repeatedly shaken up with water, acidulated, and slightly warm. The water separated from the residue was filtered, and in the clear and colourless filtrate the taxine was precipitated by ammonia or fixed alkali, in snow-white bulky flakes. When washed and dried over sulphuric acid, it forms a white crystalline powder, which is scarcely soluble in distilled water, readily soluble in acidulated water, alcohol, ether, chloroform, benzene, and carbon disulphide, insoluble in petroleum and ether. It has no smell, but a very bitter taste. Pure concentrated sulphuric acid reddens it; nitric, hydrochloric, and phosphoric acids dissolve it without change of colour. With most of the reagents characteristic of alkaloids—tannic acid, phosphomolybdic acid, potassio-mercuric iodide, potassio-cadmie iodide, potassio-bismuthic iodide, iodo-potassic iodide, potassio-argentic cyanide, potassic bichromate, picric acid—it yields, in an acid solution, amorphous precipitates. Platinic chloride, auric chloride, mercuric chloride, potassio-platinous cyanide are not precipitated. It does not form crystallised salts with the ordinary acids. It is nitro-genous (evolves ammonia when heated with freshly ignited soda-lime), melts at 80° , and burns without residue when heated more strongly.

Taxine is present in the leaves in larger quantities than in the seeds of the yew tree. D. B.

On the Alkaloids of Celandine (*Chelidonium majus*). By E. MASING (*Arch. Pharm.* [3], viii, 224—228).—Celandine contains two alkaloids, chelidonine and chelerythrine (sanguinarine), which form with Mayer's iodide of mercury and potassium, insoluble salts having, in the case of chelidonine, the formula $C_{19}H_{18}N_2O_3I.H_2I_2$. These alkaloids were estimated at given intervals in the growth of the plant by extracting with alcohol of 75 per cent. containing a little acid, and titrating with Mayer's solution. The chelerythrine, $C_{19}H_{17}NO_4$, is calculated as chelidonine. A long table of results is given, including determinations of the amount of alkaloids every few days from May to September. The general results are: a diminution in the total amount of alkaloids before flowering, and a marked increase after a few days. The young plant gathered in autumn shows a regular increase of alkaloids. This may be explained by assuming the alkaloids to be the immediate precursors of the albumin, and that they are gradually transformed into albuminous substances. The weather is also an important factor in the content of alkaloids. In rainy weather the consumption is greater than the production, and the percentage is decreased; while in fine sunny weather consumption and production are nearly in equilibrium, the production having a slight advantage. These changes are more noticeable in the root than in the leaf. A good soil influences the formation of alkaloids, for plants grown in a garden were found to contain double the amount of alkaloids found in wild plants.

The largest amount of alkaloid is 1.09 per cent., and the smallest 0.27 per cent. The average appears to be about 0.6 per cent.

W. R.

Emodin from the Bark of *Rhamnus Frangula*. By C. LIEBERMANN and M. WALDSTEIN (*Deut. Chem. Ges. Ber.*, ix, 1775—1778).—Frangulin, which Merck prepared from old bark, was found to be identical with emodin, $C_{15}H_{10}O_6$, which is a derivative of methylanthracene. Faust's frangulin is probably also derived from this hydrocarbon, and its formula would then be $C_{15}H_{10}O_4$, and it would stand in the same relation to emodin as alizarin to the purpurins.

C. S.

A new Glucoside in the Flowers of *Cichorium Intybus*. By R. NITZKI (*Arch. Pharm.* [5], 4, 327—337).—The dried flowers were exhausted with ether and alcohol.

The glucoside crystallises in long colourless needles, insoluble in ether, easily soluble in hot water and alcohol, also in ammonia; the solution is intensely bitter. The glucoside melts at 250—255°; it is decomposed by boiling with dilute hydrochloric acid, apparently in accordance with the equation:—



Further experiments are promised.
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M. M. P. M.
2. K

The Volatile Oil from Styrax. By J. H. VAN'T HOFF (*Bull. Soc. Chim.* [2], xxv, 175—177).—The author confirms the observations of Berthelot that this oil rotates the polarised ray to the left, but finds that this power is due, not to styrolene, but to a compound, $C_{10}H_{18}O$ or $C_{10}H_{16}O$, to which he gives the name *styrocamphene*.

This body is contained in very small quantity in styrax (not more than $\frac{1}{50}$ per cent.). It appears to boil between 170° and 180° and to solidify at about -10° ; with bromine a substitution-product is formed having a different odour to the addition-product of bromine and styrolene. It has a powerful lævorotatory power (-30° at least).

The identity of styrolene and cinuamene maintained by E. Kopp is therefore not affected by Berthelot's observation. W. H. P.

Patchouli-camphor. By J. DE MONTGOLFIER (*Compt. rend.*, lxxxiv, 88—90).—Essence of patchouli, when kept for some time, deposits a well crystallised substance known as patchouli-camphor. It forms regular pyramidal hexagonal prisms, some almost like spheres, from the rounding of the faces. They are always composed of a prism and a pyramidal summit, and do not exhibit hemihedry. The inclination of the faces to each other is 120° , and to the summit $121^{\circ} 24'$. They have no rotatory power for polarised light. When liquid the camphor deviates polarised light; $(\alpha)_D = -118^{\circ}$; $D =$ nearly 1. The rotatory power remains constant when the camphor is dissolved in alcohol of 95 per cent., but diminishes considerably on dilution. If e be the proportion by weight of substance in solution,

$$(\alpha)_D = -124^{\circ} 5 + 21 e.$$

The dispersion is nearly the same as that of quartz or of sugar; $(\alpha)_D = -10^{\circ} 37'$ and $\alpha_{\gamma} = -11^{\circ} 45'$. The crystals, which have the formula $C_{15}H_{22}O$, fuse at 59° and remain liquid for a long time. The hydrocarbon, which has the formula $C_{15}H_{24}$, is easily prepared from the camphor by the action of acids, but the best method is to heat the camphor to 100° for some hours with a mixture of glacial acetic acid and acetic anhydride. The upper layer consists of the hydrocarbon. It boils at 252 — 255° under 743 mms. pressure. It has been named *patchoulin*. It has no smell when pure, but oxidises easily and acquires a resinous smell. Its density is 0.946 at 0° , and 0.937 at 13.5° . It turns the plane of polarised light strongly to the right; -7.54° for the line D, and -8.48° for the transition tint. Its dispersion is therefore equal to that of quartz, and its molecular rotatory power is $(\alpha)_D = -42^{\circ} 10'$. It does not combine with hydrochloric acid, and is destroyed by nitric acid. It most resembles essence of cubebs, but differs from it in not combining with hydrochloric acid. W. R.

Colouring Matter of Viridic Acid. By DR. CROCH (*Bull. Soc. Chim.* [2], xxvi, 450).—Viridic acid does not exist in coffee ready formed, but is produced by the action of oxygen and moisture. Rochleder found no nitrogen in this substance. The author recommends this perfectly innocuous body as suitable for use in cases where it is desired to impart a green colour to articles of food. R. R.

Shell-lac and Sarcosinic Acid. By J. HERTZ (*Arch. Pharm.* [3], viii, 234—251).—This variety of shell-lac was obtained from Mexico, where it is known as “Soma de Sonora,” and called by the Indians “Arré.” It exudes from the *Mimosa coccifera*, the native name for which is Tzinacaa cuitlaquahuil. It has an astringent, bitter taste, and a yellowish or brownish colour. It is used as a remedy for diarrhoea and uterine discharges.

East Indian shell-lacs are treated with water, before they are delivered to the European market, to extract an acid substance and a red dye, which forms 10 p. c. of the weight of the crude gum.

The American specimen lost 6 p. c. of its weight on treatment with hot water. It was then treated with alcohol, which dissolved about half; the solution, on evaporation, left a transparent, brittle residue, which had all the appearance of good shell-lac. The portion which refused to dissolve in alcohol was soluble in boiling potash with a fine red colour; on addition of acid the solution became colourless, and a yellowish-white resin separated, which was partially soluble in alcohol. These reactions correspond with those of shell-lac.

The aqueous solution contained two substances,—a colouring matter and an acid body. The colouring matter was removed by lead acetate, and the filtrate evaporated after removal of the lead. The colouring matter was soluble in water with a fine red colour and insoluble in alcohol and in ether. It could not be obtained in a crystalline state. Its solution had a strong acid reaction and showed a strongly acid reaction. The filtrate from the colouring matter deposited crystals, easily soluble in water and insoluble in alcohol and in ether. They were purified by solution in boiling aqueous alcohol, from which they deposited as a powder on cooling. The formula of the acid was found to be $C_5H_7NO_2$, and it was named sarcosinic acid.

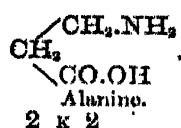
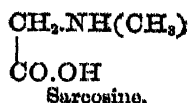
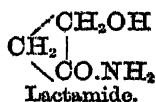
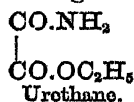
The *barium salt* is an amorphous powder, soluble in water but not in alcohol.

The *silver salt*, $C_5H_6NO_2Ag$, forms yellowish-white nodules, and is reduced on exposure to light.

The *sodium salt* crystallises with 6 molecules of water, and forms colourless hexagonal tables.

The *calcium salt* crystallises with one molecule of water, and is an amorphous powder.

The acid does not evolve ammonia when boiled with caustic soda, but on heating with soda-lime it does. It melts at 195° , and chars at a higher temperature without subliming. The acid is isomeric with alanine, sarcosine, lactamide, and urethane. The two latter, however, are indifferent bodies; lactamide when heated with soda decomposes into lactic acid and ammonia; urethane into carbonic anhydride, ammonia, and ethyl alcohol. Sarcosine unites only with acids, and it is doubtful whether it is an amido-acid; it evolves methylamine on ignition with soda-lime. Alanine, when treated with nitrous anhydride, yields lactic acid. These bodies are assumed therefore to have the following constitution:—



Sarcosinic acid appears to be more nearly related to sarcosine and alanine than to lactamide or urethane; yet sarcosine is a base, while sarcosinic acid is a true acid. The acid, however, was found to form a hydrochloride and nitrate. With nitrous anhydride nitrogen was evolved and lactic acid was formed. The acid therefore has great analogy to lactic acid, from which it differs only in taste, crystalline form, and marked acid properties. The author attributes to it the same constitutional formula as to alanine, but intends to attempt to prepare it synthetically to decide wherein the difference lies.

E. Reichart attributes to it the formula $\begin{Bmatrix} \text{CH}_3\text{NH}_2 \\ \text{CH}_2\text{COOH} \end{Bmatrix}$ W. R.

On Cotoïn. By J. JOBST (*N. Rep. Pharm.*, xxv, 23; *Chem. Centr.*, 1876, 167).—This substance was prepared in the following manner:—Coarsely-powdered coto-bark is exhausted with ether until the latter is completely saturated. The ethereal extract is evaporated to one-tenth of its volume on a water-bath, transferred whilst hot to a porcelain dish, and mixed with 6 parts of warm petroleum ether. After evaporating off the ethylic ether, large quantities of resin are deposited. The upper clear liquor is drawn off into another vessel and allowed to crystallise. With the crystals a small quantity of resin is still separated, the latter, however, adheres firmly to the bottom of the crystallising vessel, so that the crystals may easily be poured off. The crystalline mass is collected on a filter, pressed, and recrystallised several times from hot water. Cotoïn thus obtained forms white, light crystals, which may be recognised by the eye, or better under the microscope, as well-formed prisms. It possesses the hot taste of the bark, is difficultly soluble in cold water, more readily soluble in hot water, alcohol, ether, chloroform, and bisulphide of carbon. It dissolves readily in benzene and petroleum ether, but is easily obtained in large, yellow prisms by crystallisation from alcohol. It melts at 124°. Alkalis dissolve it with yellow colour, acids reprecipitate it from these solutions; concentrated nitric acid gradually dissolves it in the cold, very quickly when warmed, forming a blood-red solution. Concentrated sulphuric acid gives a brownish-yellow solution, hydrochloric acid a pure yellow solution. Its aqueous solution is neutral to litmus paper. When cold it reduces salts of gold and silver. Neutral acetate of lead does not produce a precipitate, whilst the basic acetate forms a yellow precipitate. Iron salts produce in dilute solutions a brownish-red coloration, in concentrated solutions a blackish-brown precipitate. Fehling's solution is reduced slowly whilst cold, quickly when hot. The composition of cotoïn is represented by the formula $\text{C}_{21}\text{H}_{20}\text{O}_6$. By precipitating an aqueous solution of cotoïn with basic lead acetate, a precipitate was obtained which, after being dried at 130°, had the composition $\text{C}_{21}\text{H}_{20}\text{O}_6 \cdot 2\text{PbH}_2\text{O}_2$. Cotoïn belongs to the group of chemically indifferent substances.

D. B.

Coto-barks and their Crystalline Constituents. By J. JOBST (*Deut. Chem. Ges. Ber.*, ix, 1633—1634).—A short time ago (see last abstract) the author isolated from the coto-bark of Bolivia a crystalline substance, called cotoïn, which, on account of its constipating

action, was soon introduced into medicine. A new sample of the bark which he since obtained showed some differences, and does not contain cotoïn but a similar body, which is much less soluble and does not possess the pungent taste of cotoïn. This paracotoïn has, however, similar but weaker medicinal properties. C. S.

The Derivatives of the Bile-acids. By J. LANG (*Bull. Soc. Chim.* [2], xxv, 180—183).—*Salts of Taurine.* The silver salt, $C_2H_5NSO_3Ag$, may be prepared by boiling a solution of taurine with silver oxide. It crystallises in tabular crystals which blacken on exposure to light, and are easily soluble in water but insoluble in alcohol and ether.

The mercury salt, $(C_2H_5NSO_3)_2Hg$, may be obtained by the action of a cold solution of taurine on oxide of mercury. It is a white powder, nearly insoluble in cold water, and but slightly soluble in boiling water.

The neutral lead salt, $(C_2H_5NSO_3)_2Pb$, is formed by dissolving one molecule of plumbic oxide in a solution of two molecules of taurine. It crystallises in white needles, easily soluble in water.

The basic lead salt, $2[(C_2H_5NSO_3)_2Pb] + Pb(OH)_2$, is formed by saturating a cold solution of taurine with plumbic oxide; on addition of alcohol an oil is deposited which solidifies to a white crystalline mass.

The cadmium salt, $(C_2H_5NSO_3)_2Cd$, is a white insoluble powder, formed by treating oxide of cadmium with solution of taurine.

The calcium salt crystallises in needles having the formula $(C_2H_5NSO_3)_2Ca$. It is easily soluble in water.

The sodium salt, $C_2H_5NSO_3Na$, is formed by saturating an alcoholic solution of taurine with soda. It is crystalline and very deliquescent. Taurine forms a mercuric salt with separation of metallic mercury with mercurous oxide.

Chologlycollic acid, $C_{28}H_{42}O_7$, is formed by the action of nitrous acid on glycocholic acid dissolved in nitric acid. On boiling chologlycollic acid, which does not appear to crystallise, with dilute sulphuric acid, glycollic acid is formed.

The author describes the sodium, barium, and silver salts.

The action of Glycocine on Cholic acid.—These two substances, heated together to 190—200° for 12—24 hours in sealed tubes, give a fused mass easily soluble in alcohol as product. The alcoholic solution deposits a white amorphous powder, which is easily soluble in alcohol, ether and chloroform, and appears to have the composition $C_{20}H_{30}NO_4$. This body the author calls *glycodyslysine*. It appears also to be formed when glycocholic acid is heated to 200°. W. H. P.

Physiological Chemistry.

Influence of Respiration on the Metamorphosis of Tissue.

By E. PFLÜGER (*Pflüger's Archiv. f. Physiol.*, xiv., 1—38).—The author considers it certain that, although in respiring pure oxygen, four times as much oxygen is brought to the lungs and blood as under ordinary circumstances, nevertheless the intensity of the internal combustion in the animal body remains the same. He cites some experiments made by him some time since on rabbits, in which he found that the absorption of oxygen is the same in ordinary respiration as during the most active artificial respiration. The ratio of quantity of carbonic acid excreted in ordinary respiration to that exhaled during apnoea produced by artificial respiration in the proportion of 2 to 3, indicating that in the latter state the carbonic acid passes off more rapidly by diffusion, without the production of it undergoing any change. Experiments in which the tissue-metamorphosis is estimated only by the excretion of carbonic acid, are, the author thinks, very liable to mislead. He considers the absorption of oxygen a much more trustworthy means of estimating the tissue-change. The rest of this paper is devoted to an elaborate criticism of the opposing experiments of Lossen and those of Berg on this subject,—the former believing that he has proved that the excretion of carbonic acid is diminished by an increase in the number of respirations per minute, and the latter having found an increase in the carbonic acid exhaled under the same circumstances. Both these results the author considers false, and maintains that, when correctly interpreted, they leave scarcely any doubt regarding the correctness of the law: That the respiratory-mechanism has no influence on the amount of the total tissue-metamorphosis.

E. C. B.

Influence of Respiration on the Metamorphosis of Tissue.

By DITTMAR FINKLER and ERNST OERTMANN (*Pflüger's Archiv. f. Physiol.*, xiv, 38—72).—The authors having made numerous experiments on rabbits, arrive at the following conclusions:—

1. Artificial respiration and the existence of apnoea are not accompanied by any alteration either in the consumption of oxygen or in the formation of carbonic acid; the tissue-metamorphosis therefore remains unchanged, and this, in spite of the altered conditions under which the tissues are placed from the changed mode of respiration, the tension of the carbonic acid being diminished by its free escape, and that of the oxygen probably increased from a more ready entrance of that gas into the blood. This is a further confirmation of Pflüger's law that the regulation of the consumption of oxygen is determined only by the cell, and not by the amount of oxygen or carbonic acid in the blood, or by the mode of respiration.

2. At the commencement of the artificial increase in the respiratory movements there is an apparent diminution, and at the close of the same an increase, in the consumption of oxygen. This is explained by the alteration in position of the diaphragm and thorax.

3. The excretion of carbonic acid is greatly increased at the commencement, and much diminished after the close of the artificial respiration. This is owing to the fact that the escape of carbonic acid from the blood is in one case much facilitated, and in the other greatly hindered; its formation in the tissues remains unchanged.

4. Venous blood has no characteristic colour during apnoea. It appears brighter the more sparing the ventilation of the lungs and the more energetic the action of the heart. In the authors' experiments, the external jugular vein having been cleaned, the blood in it appeared dark, but as soon as the animal was immersed in a warm bath (in order to keep its temperature constant) the blood in the vein became bright red. This the authors consider due to two causes: First, the capillaries of the skin being dilated, more blood flows through them in a given time, so that it reaches the veins in a less reduced condition; secondly, the respiration being more frequent and the exchange of gases in the lungs more complete, the blood becomes more highly charged with oxygen in the lungs. E. C. B.

On Isopepsin. By DITTMAR FINKLER (*Pflüger's Archiv. f. Physiol.*, xiv, 128—130).—The author controverts the statement of E. Salkowski in No. 21 of the *Centralblatt f. d. Medicin. Wissensch.* for 1876, that the so-called action of isopepsin is really only the action of hydrochloric acid, and that a true digestion occurs only when fresh pepsin is used. Isopepsin is the name the author has applied to a modification of pepsin produced by the application of heat to that body. The author holds that isopepsin produces a true digestion, which, on account of its being abnormal, is of importance not only theoretically, but also practically. E. C. B.

Experiments on the Coagulation of Fibrin. By A. SCHMIDT (*Compt. rend.*, lxxxiv, 78—80).—In 1861 the author published results of experiments on the coagulation of fibrin. He is now in a position to explain the reason of that coagulation. It is owing to a substance named by him *fibrogenic substance*. Fibrogenic and fibroplastic substance, separated from the liquids which contain them, and dissolved in water by means of a sufficient quantity of salt, coagulate when mixed together. These two substances are separated from the liquids which contain them by identically the same methods. 1st. By adding alcohol to the liquids till a precipitate begins to form. The precipitation requires two days and is never complete. 2nd. By diluting the liquid with 15 times its bulk of water, and saturating it with dilute acid. The precipitate contains all the fibrinoplastic substance. 3rd. Common salt is added to saturation. The precipitates obtained dissolve in water, owing to the salt which they contain. 4th. By neutralising the liquids and separating the salts by dialysis, and passing carbonic anhydride for a short time through the dialysed liquid. The salt is separated from the filtrate by rapid dialysis, and the carbonic anhydride, by placing the liquid in a vacuum. The liquid does not coagulate till the separated substances have been added. The coagulation is really a process of fermentation; the ferment, however, has no separate existence, but is formed when the liquids are removed from

their natural spheres. The ferment is formed in cells containing protoplasm; in the white blood-corpuscles, in lymph, chyle, and pus, and perhaps generally in connective tissue. It does not occur in the living body, but is formed by decomposition in the corpuscles, immediately on their exit from the body. Its formation is impeded by a low temperature, and almost completely checked by strong solutions of neutral salts of the alkalis, and especially by magnesium sulphate. The fermentation can, however, be induced by diluting the liquid.

W. R.

Origin and Accumulation of Glycogen in the Animal Organism. By S. WOLFFBERG (*Zeitschr. f. Biologie*, xii, 266—314).

—The author discusses the views and experimental researches, on this subject, of Claude Bernard, Voit, Pettenkofer, Valentin and Aeby, Bauer, Naunyn, Dock, Luchsinger, Salomon, and others, and concludes, from these and his own results, that glycogen is an intermediate decomposition-product of albumin in the animal organism, the amount formed in any given case being dependent on the quantity of albuminoids thus altered, and on the presence of various other substances, especially carbohydrates, which influence (by their greater or lesser power of resisting the decomposing actions of the organism) the rate at which the glycogen, when once formed, becomes further changed.

Fowls were fed for about 10 days on a powder composed of dried horseflesh, from which all non-muscular tissue had been carefully eliminated, previously to the feeding, and they were then starved for 24 hours or more. The powder contained, when air-dry, 7·12 per cent. moisture, and 100 parts of dry powder contained 2·07 per cent. of fat. After feeding for a certain time, the fowls were killed by a blow on the head; the liver was excised as speedily as possible, weighed, and cut up in boiling water. After a few minutes the fragments were pounded in a hot mortar, and boiled with water, until the fluid showed no more opalescence. The liquid was then rapidly evaporated on the water-bath, cooled, and treated with hydrochloric acid and Brücke's re-agent; to the filtrate, three times its volume of alcohol was added, and after 24 hours the precipitated glycogen was filtered off and weighed. The pectoral muscles were treated in the same way, rubbing in the mortar excepted. In this way, in four experiments, the following results were obtained:—

	(1.)	(2.)	(3.)	(4.)
Weight of fowl in grams before fasting	—	1653	1204	1020
Weight of fowl in grams after fasting	1320	1585	1139	944
Weight of fowl just before killing	1455	1718	1092	986
Grams of powder given per diem	44—50	40—50	30—40	30—40
Weight of liver in grams	28·65	41·1	70·1	18·4
Do. glycogen in liver	0·446	0·598	0·102	0·041

	(1.)	(2.)	(3.)	(5.)
Percentage of glycogen in liver	1.56	1.45	0.145	0.22
Percentage of glycogen in pectoral muscle	0.251	0.454	0.211	0.162
Length of time intervening between last feeding and death.....	10 hrs.	10½ hrs.	17 hrs.	24 hrs.

The first two cases show that feeding with albuminoids can develop considerable quantities of glycogen; whilst the latter two indicate how rapidly this glycogen can, under favourable circumstances, again disappear; as, for example, when the animal is kept without food.

Another set of experiments was made when the fowls were fed with the same powder of horse-flesh and varying quantities of grape-sugar, the duration of the feeding, however, being only a single day, and the animals being starved for three days previously. The following results were obtained:—

Grams of food given.		Time intervening between last feeding and death.	Grams of glycogen in liver.
Albuminoids.	Sugar.		
1. 8.0	30.0	24 hours	0.107
2. 20.0	40.0	16½ "	0.375
3. 20.0	60.0	17½ "	1.441
4. 20.0	90.0	14 "	1.757

In yet another series, varying quantities of albuminoids were given along with a constant amount of sugar, the mode of feeding, &c., being the same as in the second of the above series. The following end results were obtained:—

Grams of food given.		Time intervening between last feeding and death.	Grams of glycogen in liver.
Albuminoids.	Sugar.		
20	90	14 hours	1.757
50	60	14 "	1.840
30	60	14½ "	0.821
30	60	16½ "	0.631
8	60	20 "	0.474

C. R. A. W.

Critical Experiments on the Formation of Sugar in the Blood. By C. BERNARD (*Ann. Chim. Phys.* [5], ix, 207—258).—The author shows that sugar is a vital constituent of the blood, in which it is present in quantities varying from 1 to 3 parts per 1000. After death it rapidly disappears, and the same occurs in blood after its withdrawal from the body. The blood of a dog, analysed at successive intervals after its withdrawal from the veins, gave the following results:—

1.	Analysis made immediately	1.07 parts per 1000.
2.	" after ten minutes.....	1.01 "
3.	" " thirty "	0.88 "
4.	" " five hours	0.44 "
5.	" " twenty-four hours ..	0.00 "

Sugar is equally present in the blood of carnivorous and herbivorous animals, and is quite independent of the nature of the food. This is shown by the following results:—

	Sugar per 1000 parts.
Rabbits fed on herbs	1.25
	1.40
	1.32
Dogs fed on meat.....	1.45
	1.10
	1.24
Rabbit—fasting	1.17
Dog in good health—fasting	1.21
Dog in fever—fasting	1.41
Man in good health.....	1.17

Arterial blood contains more sugar than venous blood. An examination of arterial and venous blood from three dogs gave the following results:—

	Sugar per 1000 parts.	
	Arterial blood.	Venous blood.
Dog I.	1.45	0.73
„ II.	1.24	0.99
„ III.	1.17	0.88

By comparing the quantities of sugar found in the blood at different parts of the system, the author has traced its production to the liver.

H. H. B. S.

Urea in Blood. By P. PICARD (*Compt. rend.*, lxxxiii, 991—993).

—For estimating the quantity of urea in blood, the following process was adopted by the author:—50 grams of sodium sulphate are added to 50 grams of the blood, and the mixture is raised to the boiling point, with constant stirring. The loss of the original weight is made up by the addition of distilled water, and the liquid, having been pressed out of the precipitate, is filtered. Of the clear and colourless fluid, 50 grams are taken and heated with 20 c.c. of hydrochloric acid, and to the mixture 20 c.c. of nitric acid are subsequently added. The carbonic acid gas, resulting from the decomposition of the urea, is absorbed by a solution of baryta in a suitable apparatus. The barium carbonate thus formed is decomposed by hydrochloric acid, and the volume of carbonic acid gas liberated is measured, and from it the amount of urea is deduced.

R. R.

Behaviour of Phenols in the Animal Body. By E. BAUMANN and E. HERTER (*Deut. Chem. Ges. Ber.*, ix, 1447—1449).—It has already been shown that common phenol is changed by the animal organism to phenylsulphuric acid. Cresol behaves in the same way; the sulphates of the urine diminish or disappear, being replaced by cresylsulphuric acid, which is identical with that found in horses' urine. Thymol and resorcin gave similar results, but not aromatic oxyacids; while their amides or ethers, as winter-green oil, also give rise to the formation of conjugated sulphuric acids.

C. S.

Behaviour of the Terpenes in the Organism. By R. V. DEN FELDEN and E. BAUMANN (*Deut. Chem. Ges. Ber.*, ix, 1746).—The pure hydrocarbons do not form conjugated sulphuric acids, which are produced only by oils containing oxygen, or are phenols. C. S.

Action of Fuchsine introduced into the Stomach and the Blood. By V. FELTZ and E. RITTER (*Compt. rend.*, lxxxiii, 984—985).—Daily injection of small quantities of pure fuchsine free from arsenic into the stomach of dogs, resulted in the presence in the urine not only of the colouring matter itself, but of a certain quantity of albumin, varying from 5 to 50 centigrams.

When the fuchsine was injected into the venous system, albumin and fatty granular cylinders were observed in the urine; in one of the dogs a single injection caused an undoubted attack of dropsy.

F. D. B.

Chemistry of Vegetable Physiology and Agriculture.

Examination of the Sun-flower (*Helianthus annuus*.) By G. C. WITTSTEIN (*Arch. Pharm.* [5], iv, 290—293).—This flower is largely cultivated in the interior of Russia and in Hungary.

From a Bavarian *tagwerk* (= 3407 square meters) about 16,000 plants are obtained, each weighing 5 to 5½ kilos. The total weight consists of:—Stalks, 40,000 kilos; leaves, roots, and blossoms, 40,000 kilos; and seed, 4,000 kilos. The ash of leaves, roots, stalks, and blossoms (without seeds) contained 62 per cent. of K_2CO_3 : the total potassium carbonate obtained by evaporating an aqueous solution of the ash to dryness amounted to 82·8 per cent. The total potash obtainable from the 16,000 plants would amount to about 1,100 kilos.

About 22 per cent. of oil may be extracted from the seeds by means of ether, representing about 850 kilos. from the 16,000 plants.

M. M. P. M.

Sugar in the Leaves of Beetroot. By J. PIERRE (*Compt. rend.*, lxxxiii, 1075—1077).—From 158 kilograms of beetroot leaves, the author expressed 34 litres of juice, which, after fermentation, yielded by distillation 275 c.c. of alcohol of 68°, and 135 c.c. of liquid at 8°, centesimal. From these and other data he calculates that the leaves of 1 hectare of beetroot might yield 173 litres of absolute alcohol, and that therefore these leaves, at the time when the beetroots are pulled up, contain about 350 kilograms of sugar.

R. R.

Ash of "*Euphorbia amygdaloides*, and of "*Herniaria glabra*." By G. O. WITTSTEIN (*Arch. Pharm.* [5] 4, 341—2).—*Euphorbia*.—1. From siliceous soil. Total ash = 5·936 per cent. (in air-dried plant).

K ₂ O.	Na ₂ O.	Na(with Cl).	CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .
33.441	1.443	1.155	15.121	4.371	1.057	0.413
Mn ₂ O ₄ .	Cl.	SO ₃ .	PO ₄ .	SiO ₂ .	CO ₂ .	
0.344	1.781	7.135	5.414	12.093	15.832.	

2. From another siliceous soil. Total ash = 4.850 per cent.

K ₂ O.	Na ₂ O.	Na(with Cl).	CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .
15.362	0.298	0.540	33.135	4.796	1.325	0.656
Mn ₂ O ₄ .	Cl.	SO ₃ .	PO ₄ .	SiO ₂ .	CO ₂ .	
trace.	0.836	3.733	4.474	8.634	25.970.	

Herniaria.—1. From siliceous soil. Total ash in air-dried plant, 7.132 per cent.

K ₂ O.	Na ₂ O.	Na(with Cl).	CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .
24.380	4.110	1.702	14.349	6.300	1.321	1.033
Mn ₂ O ₄ .	Cl.	SO ₃ .	PO ₄ .	SiO ₂ .	CO ₂ .	
—	2.624	1.717	9.729	14.445	17.694.	

2. From dolomitic soil. Total ash, 6.622 per cent.

K ₂ O.	Na ₂ O.	Na(with Cl).	CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .
8.680	3.860	0.691	30.400	14.839	1.755	0.430
Mn ₂ O ₄ .	Cl.	SO ₃ .	PO ₄ .	SiO ₂ .	CO ₂ .	
	1.066	1.746	8.421	6.367	21.505.	

M. M. P. M.

Study of the Ferments contained in Plants. By C. KOSMANN (*Journ. Pharm.* [4], xxii, 335—340 and 420—423).—There appears to exist in the buds of trees and young leaves of many plants a natural ferment which is capable (1) of transforming cane-sugar into glucose, (2) of converting starch into dextrin and glucose, and (3) of resolving a glucoside, such as digitalin, into glucose and digitaliretin. The method adopted to show the presence of the ferment was as follows:—The buds or young leaves were chopped and macerated in cold water; after twelve hours the liquor was strained off, filtered, and a portion warmed with Fehling's solution to see if any precontained glucose was present. 1.5 to 4.0 grams of sugar were then added and the solution allowed to remain for some hours at a temperature of 18° to 30°. Generally at the end of 24 hours the whole of the sugar was inverted, and a syrup of glucose could be obtained by evaporation, which had a powerfully reducing action upon the copper solution. Instead of sugar starch-paste was sometimes used, which, when acted upon, was converted as above mentioned. No gas was evolved in these experiments, on the contrary oxygen was absorbed: a microscopic examination of the deposits which occurred also revealed the presence of much organic life.

The ferment was proved to exist in the following plants:—Buds of *Ulmus campestris*; *Populus nigra*; *Quercus pedunculata*; and *Corylus avellana*. In the flowers of *Cornus sanguinea*, and *Prunus spinosa*. In the young leaves of *Chelidonium majus* and *Digitalis purpurea*.

An infusion of digitalis leaves reduced a considerable quantity of digitalin on exposure to sunlight, resolving it into glucose and digitalextrin. The latter substance was collected as a precipitate, dissolved in alcohol, and submitted to suitable tests whereby it was recognised.

Extraction and Purification of the Ferment contained in Digitalis.—To a concentrated infusion of the young and fresh leaves, its own volume of strong alcohol was added. After twelve hours the greyish-white precipitate which had fallen was collected, washed, and dried. It was then redissolved in water, the solution filtered from a little insoluble matter, and again precipitated by the addition of alcohol. The white precipitate was washed with alcohol, and then dried on glass. The dry substance was greyish-white, granular, soluble in water, and was not rendered blue by iodine. Under the microscope it presented the appearance of granules adhering to one another. It possessed eminently the power of decomposing cane-sugar, starch-paste, and soluble digitalin, acting thus quite as energetically as a strong infusion of the leaves of the fresh plant. J. W.

Analytical Chemistry.

Blowpipe Reactions. By E. J. CHAPMAN (*Chem. News*, xxxv, 13, 26).—1. *Reactions of Metallic Thallium before the Blowpipe.*—Thallium heated in a closed tube melts easily, and a brownish vitreous slag, becoming pale-yellow on cooling, forms round the globule. In the open tube the glass is strongly attacked, and a small amount of a greyish-white sublimate is formed, which shows faint iridescence. On charcoal thallium melts easily, volatilising in white fumes, colouring the flame green; a small amount of oxide and trioxide is formed on the support, which deposit, if it be formed in porcelain, is brownish-black, and appears to consist of Tl_2O_3 . With borax and phosphorus-salt colourless glasses are formed, which become grey and opaque in the reducing flame; with platinum, gold, antimony, and bismuth, a brittle, dark-grey globule is formed; with silver and copper the button is malleable.

2. *Opalescence produced by Silicates in Phosphorus salt.*—Silicates dissolved in phosphorus-salt form a "silica skeleton," which, if the blast be continued long enough, exhibits an opalescence on cooling; this is due to precipitation of the silica, as may be proved by producing a silica bead dissolved in borax, which becomes opalescent on the addition of phosphorus-salt.

3. *Reactions of Chromium and Manganese with Sodium Carbonate.*—Sodium chromate and manganate enamels resemble one another, but the chromate enamel is yellowish-green after exposure to the

oxidising flame, while the manganate is greenish-blue when cold. If, however, vitrified boric acid be added to the glass until all the carbon dioxide is expelled, a clear glass is obtained; a chrome glass will be green, whereas the manganese glass will be violet.

4. *Detection of Cadmium in presence of Zinc.*—The substance to be tested, if in the metallic state, must be roasted, the resulting powder fused with borax, and acid sulphate of potassium added: the head is then treated with boiling water, and a bead of potassium sulphide, prepared by heating acid sulphate of potassium on charcoal is added; if cadmium be present a yellow precipitate is formed.

5. *Solubility of Bismuth Oxide in Sodium Carbonate.*—Bismuth oxide dissolves readily in fused sodium carbonate, forming a glass which is a clear yellow while hot, but gradually assumes a yellowish-brown tinge, and finally becomes pale-yellow and opaque when cold. As regards their solubility by fusion in sodium carbonate, metallic oxides fall into three groups (1) easily soluble, PbO , Bi_2O_3 , BaO , &c.; (2) slightly soluble, Mn_2O_3 , CoO , &c.; (3) insoluble, Fe_2O_3 , Ce_2O_3 , NiO , CaO , MgO , &c.

6. *Detection of Bromine.*—The bromide is rendered soluble by fusion with sodium carbonate, then dissolved in water, and to the clear solution silver nitrate is added: the silver bromide thus formed is fused with acid sulphate of potassium in a test-tube, when the silver bromide separates as a blood-red globule, becoming yellow on cooling; this exposed to sunlight turns green.

Silver chloride so obtained melts into an orange-red globule, cooling to a white mass, and becoming grey in sunlight. The iodide forms whilst hot a black bead, changing to amethyst-red, and finally to dingy-yellow when cold. A mixture of chloride and iodide assumes a greenish tint.

Detection of Carbonates.—A silicate is easily distinguished from a carbonate, sulphate, phosphate, borate, fluoride or chloride, by the difficulty with which it dissolves in phosphorus-salt; a carbonate may be as readily distinguished from any of the above by the effervescence which ensues when it is introduced into a molten phosphorus-salt bead.

E. W. P.

On the Decomposition of some Ammonium Salts by Potassium and Sodium Salts. By H. O. DIBBITS (*Zeitschr. Anal. Chem.*, 1876, 245—250).—Dibbits has already shown (*Pogg. Ann.*, 150—260) that when solutions of the salts of ammonium are boiled they lose ammonia, the quantity lost depending on the nature of the salt, as well as on the concentration and volume of the solution and amount of water evaporated. The fact that the loss of ammonia varied in amount with the particular ammonium salt present showed that this result might be used to determine the nature of any ammonium salt contained in a solution, together with a salt of potassium or sodium salt. By these means it might be ascertained, for instance, whether, when solutions of equivalent quantities of ammonium sulphate and potassium chloride are mixed, the ammonium is present in the form of sulphate or of chloride, or both, because were the ammonium

present in the first form, it would lose more ammonia on boiling than if present in the second form.

Equivalent proportions, or multiple ratios of the equivalent proportions (decigrams per litre) of the different salts were dissolved in 200 c.c. of water, two volumes of 50 c.c. each successively distilled off, and the quantity of ammonia in the distillates determined. When ammonium sulphate is distilled alone in this manner, it loses 9.7 milligrams of ammonia, whilst when ammonium chloride is thus treated, it loses only 1.7 milligrams of ammonia. When one equivalent of ammonium sulphate was mixed with one equivalent of potassium chloride, and the solution of the mixed salts distilled, the loss of ammonia amounted to 8.5 milligrams. When the ratio of ammonium sulphate to the potassium chloride was increased to one to two and one to five, the loss of ammonia fell to 7.9 milligrams and 7.0 milligrams respectively. On reversing the salts and employing a mixture of one equivalent each of ammonium chloride and potassium sulphate, the loss of ammonia was 8.5 milligrams.

From these experiments it appears that whether equivalent quantities of ammonium chloride and potassium sulphate, or ammonium sulphate and potassium chloride are mixed, the resulting solution possesses this property in the same degree. When one equivalent of potassium chloride is added to a solution of one equivalent of ammonium sulphate, the loss of ammonia on distillation falls from 9.7 to 8.5 milligrams, showing a partial conversion into ammonium chloride. The addition of further quantities of potassium chloride still further reduces the loss on distillation from 8.5 to 7.9 and 7.0 milligrams, showing the formation of still more ammonium chloride. Were, however, the whole of the ammonium sulphate converted into the chloride, the loss of ammonia would have fallen to only 1.7 milligrams. These experiments show, therefore, that the solution contains all four salts, namely, the ammonium sulphate and chloride and the potassium chloride and sulphate, and that the amount of ammonium sulphate preponderates, but varies inversely to the amount of potassium chloride present. Exactly similar results were obtained with ammonium sulphate, oxalate, and acetate in presence of potassium and sodium chlorides and nitrates, and in the case of the last ammonium salt, with barium chloride and nitrate.

In the same manner was studied the action of the presence of potassium or sodium sulphates upon the loss of ammonia from a solution of ammonium sulphate, and it was found that they increased the amount lost, and that the greater the amount of these sulphates present, the greater was the loss of ammonia on distillation. Analogous results were obtained for ammonia solutions undergoing spontaneous evaporation in the presence of different alkaline salts.

E. N.

New Reaction of Iodates and Iodides. By M. CORNE (*Journ. Pharm.* [4], xxii, 425).—If to an aqueous solution of an iodate there be added a few drops of water in which phosphorus has been kept, an immediate liberation of iodine results. Since both phosphoric acid and a piece of clean phosphorus are incapable of producing this

instantaneous reaction, it is probable that the liberation of iodine is due to the presence of phosphorous acid in the liquid. This assumption is strengthened by the observation that a fragment of phosphorus does liberate iodine after it has remained some days in the above-mentioned solution.

The phosphorised water is without action upon bromates, chlorates, and arsenates; neither does it react with an alkaline *iodide*. The author, however, makes use of the new reagent to detect an iodide by boiling the latter with a few drops of sodium hypochlorite, whereby it is converted into an iodate, and then adding a small quantity of the phosphorised water. An immediate liberation of iodine takes place, which may be recognised by means of starch paste or carbon sulphide in the usual manner. J. W.

Estimation of Sulphur in Coal Gas. By G. BRUGELMANN (*Zeitschr. Anal. Chemie*, xv, 175—186).—The author employs the method formerly described by him for the estimation of chlorine, phosphorus, and sulphur in organic substances, viz., burning in a stream of oxygen, and passing the products of combustion over granules of quicklime. The gas to be examined is collected over water in a large flask of some 10 litres capacity, closed by an india-rubber stopper perforated with two holes; through one of these a glass tube passes, reaching nearly to the bottom of the flask; this is connected with a reservoir by an india-rubber tube furnished with a pinch-cock, so that water can be allowed to enter at will, and expel the gas through a tube passing through the other hole in the stopper, whence it is led to a combustion tube, into which a stream of oxygen is also allowed to pass by means of a doubly perforated cork. This tube is about 12 mm. in internal diameter and 48 cms. long. The end is closed with a pellet of crumpled platinum foil occupying about 2 cms.; behind this is a layer of 10 cms. of granulated quicklime, prepared by igniting the nitrate. The tube is then filled up with fragments of quicklime, and finally a plug of broken glass surmounted by 20 cms. of finely shred asbestos, or of crumpled up platinum foil is inserted.

When the combustion of the gas is completed (which for 10 litres requires $1\frac{1}{2}$ to 2 hours), the quicklime at the further end of the tube is extracted for a length of about 2 cms., dissolved in acid, and tested for sulphate; if none be found the operation has been successful, and the rest of the lime is dissolved in acid, and the sulphate precipitated by barium in the usual way. If, on the contrary, sulphate be found in the last 2 cms. of quicklime, it is probable that some sulphur has escaped without conversion into calcium sulphate, and the operation should be commenced over again. C. R. A. W.

ANNIVERSARY MEETING,

March 29th, 1877.

Professor ABEL, President, in the Chair.

THE following Report was read by the President :—

At the termination of this, the 36th year of the Chemical Society's existence, I have, on behalf of its Council, to submit the following statement of its condition and affairs :—

At the last anniversary meeting, the Society numbered 881 Fellows. Of this number it has, during the past year, lost by deaths, removal, and resignations, 30 Fellows, while there have been elected and admitted into the Society 35 Fellows; so that the actual increase in its numerical strength this year is 35, the total number of Fellows at the present date being 916.

Seven foreign members have been elected during the past year, namely, Professor Bayer, Buttlerow, Cooke, Friedel, Heintz, and Thomsen, and one eminent name, that of M. Balard, has been removed from our list by death; the present number of foreign members is, therefore, 36.

The loss of Fellows by death which the Society has sustained during the past year is unusually heavy. The Fellows deceased, numbering 16, are:—T. Charlesworth, F. C. Desvignes, Henry Deacon, Paul DelaRue, David Forbes, Alexander Harvey, Jonathan Hearder, F. H. Hobler, A. S. Hobson, Charles Lambert, L. A. Lucas, Maurice Lichtenstein, George Parry, Alfred Smee, Frank Smith, and Thomas Heathcote Wyndham.

Mr. Thomas Charlesworth, of Leicester, was born in that town on December 5th, 1825. His parents were in humble circumstances; he received but a very slight education at the Great Meeting School, and at the age of nine began to work for his living at Mr. Bowmar's hosiery trimming factory, where he remained about 20 years.

In the year 1856 he commenced in a small way on his own account as a dyer and trimmer of hosiery goods, and by his industry, frugality, and aptitude, he succeeded far beyond his expectations.

His business continued to prosper until his death, which occurred on the 28th of May, 1876, from fatty degeneration of the heart.

Henry Deacon was born in London on July 30th, 1822. He left school at the age of 14, already showing a considerable taste for mechanical subjects, and was apprenticed to the then well-known firm of Messrs. Galloway and Sons of London.

Owing to a family friendship of long standing, Mr. Deacon, during his life in London, was frequently in the company of Michael Faraday, who took a great interest in him, and taught him the elements of chemistry in his own laboratory at the Royal Institution. In after life Mr. Deacon used very frequently to refer to Faraday's kindness to him, and to the influence which his teaching had upon the train of reasoning that long afterwards led to the theoretical considerations which he always maintained in connection with the chlorine process with which his name will ever be associated.

Mr. Deacon held that the theory of the parallelogram of forces, so well known in mechanics, was equally applicable to chemical forces, and contended, for example, that just as a body moving to a point in the south-east, need not first move due south, and then due east, but might pass uniformly south-east; so a substance formed by the reaction of two chemical forces may be the direct resultant of the forces, and need not be supposed to be formed only by the decomposition of some necessary intermediate body. This theory Mr. Deacon brought forward before the Chemical Section of the meeting of the British Association held in Liverpool in 1870, and maintained that the ordinary explanations of such phenomena as the production of an indefinite quantity of ether from alcohol and a small quantity of sulphuric acid, and of the manufacture of vitriol on the large scale, were unsatisfactory, and that the sulphovinic acid and the crystalline compounds necessarily formed in these reactions respectively, according to the usual explanations, though never found in working the processes, are by this theory not necessary steps at all, the ether and the sulphuric acid being the *direct resultants* of the forces in operation in each process.

During the time of Mr. Deacon's apprenticeship, Messrs. Galloway and Sons failed, and arrangements were made by which his indentures were handed over to another firm of mechanical engineers, Messrs. Nasmyth and Gaskell, of Patricroft near Manchester. Here Mr. Deacon finished his apprenticeship, and also by his ability and industry gained such approval from his masters that some years afterwards, one of them, Mr. Gaskell, joined him in partnership, and they founded the firm of chemical manufacturers now known as Gaskell, Deacon, and Company.

Mr. Deacon left Messrs. Nasmyth and Gaskell to take the post of manager at the Plate Glass Works of Messrs. Pilkington at St. Helens. A considerable amount of machinery was used in these

works, and Mr. Deacon was enabled to use to advantage the mechanical and engineering knowledge which he now possessed; he also had opportunities of carrying on the study of chemistry, as he was allowed the use of the laboratory of the firm. By hard work he rapidly improved his position in the works. Mr. Deacon's next position was as the manager of the alkali-works which were just being erected in Widnes by Mr. Hutchinson. Here he remained for some time, and then entered into partnership first with Mr. Wm. Pilkington, and then in 1855 with Mr. Gaskell, his former employer at Patricroft, for the purpose of establishing alkali-works in Widnes. Owing chiefly to Mr. Deacon's ability and energy, the works grew rapidly, and are now amongst the largest of the kind in the world.

Mr. Deacon was the patentee of the process which has already been mentioned, for the continuous production of chlorine on the large scale. Particulars of this process, and of the researches connected with it, were given by him in papers read before the Chemical Society and the British Association in 1870. Mr. Deacon's theoretical views upon the reactions involved in it were original and striking, and were the result of considerations which had occupied his mind for many years. In the use of this process on the large scale, the hydrochloric acid evolved in "saltcake" making, mixed with air, is drawn through an iron vessel filled with lumps of clay or some other suitable material which has been dipped in a solution of chloride or sulphate of copper; the chlorine formed, after passing through wash-towers to condense any undecomposed hydrochloric acid, is conducted to bleaching-powder chambers. These chambers were invented by Mr. Deacon, and consist of a series of horizontal shelves placed above one another, and the chlorine is passed backwards and forwards along them.

Mr. Deacon was a particularly public spirited man, and took great interest in the progress and welfare of Widnes. He was connected with most of the local institutions, was chairman of the first Local Board, and also at the time of his death of the first School Board.

He was made a magistrate of the county in 1865, and for many years attended very closely to the duties which devolved upon him in that capacity.

Latterly his health had not been at all good, but his friends thought that he was regaining strength, until he was seized with an attack of typhoid fever, of which he died after only a week's illness on July 23rd, 1876, at the age of 53.

Frederick Charles Desvignes was born at Vienna in 1846. He commenced his education as an artist, but his tastes soon led him to give Science the preference. He carried the study of mathematics to a high pitch, and invented several instruments for measurement and

calculation, which his mechanical skill enabled him to construct himself. Later on, he devoted himself almost entirely to chemistry, in the pursuit of which he evinced both ability and originality. Having gone through a course of study at the Pharmaceutical Society; he had established a laboratory shortly before his death took place. His talents and early training had made him an accomplished linguist and musician; and he bid fair to become a valuable member of the Society into which he had been but recently elected.

Paul Bienvenu DelaRue, though not an original member of the Society, was among those who joined it at a very early period of its existence. He was born in the Island of Guernsey in May, 1801, and was a pupil of his late brother, Thomas DelaRue. In 1833, the late General Wilson, Director of the Imperial works at Alexandrofsky, near St. Petersburg, induced him to undertake the introduction into those works of the new method of manufacturing playing cards, invented by his brother, and he remained at Alexandrofsky until 1849, when he established himself in business in St. Petersburg. Mr. Paul DelaRue applied his chemical knowledge to perfecting the manufacture of writing inks, those made by him being held in high esteem in Russia. He left that country in 1870, and died in September, 1876, at Phrineas Lodge, Beaulieu, Invernesshire, the shooting lodge of his son-in-law, Mr. William S. Winans. Mr. DelaRue was a man of most genial disposition, and greatly beloved by the poor.

David Forbes, brother of the late Professor Edward Forbes, was born at Douglas, in the Isle of Man, in 1828; he was partly educated there, and subsequently at Brentwood in Essex.

At an early period, and even when at school, he showed a strong predilection for chemistry, and the allied sciences. His school days over, he was removed to the University of Edinburgh, where, in Dr. Wilson's laboratory, he laid the foundation for those chemical and physical studies which so distinguished his later years.

After working for some months in the laboratory of Dr. Percy at Birmingham, an early opportunity was afforded him of turning his chemical and scientific training to good account, for, before he was twenty, he accompanied Mr. Brooke Evans to explore the mineral resources of Espedal in Norway, and afterwards to superintend extensive mining and metallurgical works in that locality, where he remained for some years. During this period he travelled much, and had no opportunity of increasing his store of scientific knowledge, as his writings testify.

During his long residence in Norway, Forbes carefully studied the

mineralogy of the several districts of that country, with especial reference to the circumstances under which each mineral occurred, and the causes which led to its appearance, the results of his investigations being included in several papers published in 1855-57.

Forbes afterwards became a partner in the well-known firm of Evans and Askin, nickel smelters, Birmingham, and it was in connection with them that he visited Chile, Peru, and Bolivia, in search of nickel and cobalt. His investigations into the mineral resources of these countries extended over six years. During the years 1857-60, he made a special geological exploration of certain districts in South America, and amidst formidable difficulties, collected much invaluable information, part of which was communicated to the Geological Society in 1860.

From South America, Forbes made an expedition to the South Sea Islands, and spent some time in studying their volcanic formation and minerals.

During four years he traversed Chile in all directions from considerably south of Santiago, northwards up to the frontiers of Bolivia in the Desert of Atacama. He inspected all the principal, and some of the lesser, mining districts along the range of the Cordilleras; from these he collected a valuable and extensive series of minerals, including about 190 species, of which he published a list in 1865 classifying them according to the mode of their geological occurrence, in an important paper "On the Mineralogy of Chile."

Igneous and metamorphic phenomena and the resulting changes in rock-formations were among David Forbes's especial and favourite studies, and he lost no opportunity, during his extensive travels in Europe and Africa, but especially in Mexico and South America, of observing the effects of modern volcanic action, and their relation to similar phenomena in past time.

Having ample opportunities in Norway, in connection with metallurgical operations, he was enabled to submit various rocks to high temperatures and pressures for longer or shorter periods, and thus imitate metamorphic action in the production of various forms of rock-structures. The results of these experiments were partly embodied in his paper to the Geological Society in 1855, "On the Causes producing Foliation in Rocks." Bearing also on this subject are his papers "On the Chemical Composition of some Minerals from the south of Norway," "On the Igneous Rocks of Staffordshire," "On the Contraction of Igneous Rocks in Cooling," and his lecture "On Chemical Geology," delivered to this Society in 1868.

Besides his researches on the mineral characters of rocks, David Forbes devoted considerable attention to their microscopic structure, and was among the first of English geologists who directed

attention to the study of micro-geology. His paper on "The Use of the Microscope in Geology," in the *Popular Science Review*, was republished in some German periodicals, and he was in frequent communication with Professor Zirkel and other foreign geologists on this subject, with a view of ultimately embodying it in a work on Petrology, which he contemplated publishing.

Mr. Forbes was a Fellow of the Royal, the Chemical, and the Geological Societies. Of the latter he had been the active Honorary Secretary for some years past, and he officiated at a meeting of the Society very shortly before his death. As Foreign Secretary of the Iron and Steel Institute, he has prepared for six years (1871-76) careful and elaborate details of the progress of the iron and steel industries in foreign countries, in which his knowledge of languages materially assisted him. Nor did geological science and mineralogy alone interest him, for as a member of the Ethnological Society he contributed an interesting and elaborate paper "On the Aymara Indians of Bolivia and Peru."

Upwards of fifty papers have been communicated by Mr. David Forbes to the scientific societies and to scientific journals, such as the "Chemical News," the "Transactions of the Iron and Steel Institute," and the "Philosophical Magazine." Sixteen of Mr. Forbes's articles and letters have appeared in the Geological Magazine from 1866-72. They all indicate the tendency of his mind to study the bearings of chemistry on igneous and cosmical phenomena. Forbes felt that whilst in other departments of geology, Great Britain was foremost, she was far behind in the study of chemical geology, and he hoped that others might be induced to devote themselves to this most interesting and prolific branch of scientific inquiry. His views on this subject were expressed in his papers on "Chemical Geology," and on the "Chemistry of the Primeval Earth," published in 1867-68.

Forbes was a very expert blowpipe-operator, and his wonderful neatness as a chemical manipulator may be in part traced to his training and expertness in blowpipe-analysis. His paper on "The Application of the Blowpipe to the Quantitative Determination or Assay of certain Minerals," published in the "Chemical News," constituted a valuable contribution to this branch of analysis.

Forbes was a man of most resolute and determined courage and energy, of which many illustrations were furnished during his sojourn and travels in foreign countries. Thus, while living in Norway, when a revolution threatened the country in 1848, he armed and organised 400 of the men under his employment to aid the Government, a service which gained him the personal thanks and friendship of the King. Again, in South America, while foreigners journeying to the

mining districts, generally travelled with a cavalcade of servants and mules laden with provisions and comforts, Forbes, who acquired a knowledge of the language and habits of the miners and smelters with marvellous rapidity, would traverse the most distant portions of the Chilian Republic, with a single guide, and often unattended. Thus, after having been only a few weeks in Coquimbo, he had explored nearly every mineral district of importance, knowing them better than most foreigners who had resided in the country for many years.

Forbes devoted himself almost entirely to his professional and literary pursuits, and of late years took but little physical exercise, and it is to be feared that his too sedentary habits, together with the sad domestic loss he had recently suffered, depressed his spirits, and broke up a constitution, which, in the days of his travels, was as of iron, but which had of late years become enfeebled by recurrent fever caught in South America.

He died after a brief illness on the 5th December, 1876, at the age of 49.

The loss of David Forbes is keenly felt by those friends who really knew his genial and social character; whilst his scientific associates, who had hoped for the further prosecution and publication of his researches and observations on rocks and minerals, will all regret his vacant place in their midst.

Alexander Harvey, who at the time of his death was Bailie of Provan, was born at St. Unians, on February 8th, 1799. He commenced his career as a watchmaker, at which trade he worked for some years with his father, at Stirling, devoting his leisure to scientific and chiefly chemical study. While there, on an occasion of his father's absence, he contrived to light up the shop with gas, a great achievement in those days, and which led to his going to Glasgow, in 1817, as Laboratory Assistant to the late Professor Thomas Thompson. He left the University to enter the employment of Messrs. Tennant, of Rollox, and after holding a responsible position there for some years, he married the daughter of Mr. Rodger, head-manager of the Barrowfield Print Works, whom he eventually succeeded. While connected with those works, his chemical knowledge enabled him to make several important improvements in colours. In 1838 he started the dye-works at Govanhaugh, on his own account, and attended to their management until within a few years of his death, the works having gradually grown to considerable proportions. Among new colours introduced into printing and dye-works by Mr. Harvey are chrome-orange, chrome-green, and catechu-brown. But Mr. Harvey's sphere of usefulness was not confined to the development of his special branch of

manufacturing industry. He was for a considerable time connected with the burgh of Gorbals, as Commissioner and Bailie, and afterwards served the public as member of the Town Council for a dozen years, rising to the position of river bailie two years after his election to the Council. He subsequently became magistrate of the burgh, acting in that capacity for three years. On his retirement from public life, in 1863, his valuable services were acknowledged by his election to the appointment of Bailie of Provan, a very ancient post, which has, of late years, become of a purely honorary character, and is conferred as an acknowledgment of personal desert and faithful public service.

Mr. Harvey's sagacity and knowledge of science often rendered his advice on public matters of importance invaluable, while his taste and skill in all matters connected with art added to the great influence which he exercised in public affairs. The introduction of water by gravitation into Gorbals; the supply of water to Glasgow from Loch Katrine; the erection of the upper Suspension Bridge over the Clyde; the erection of an organ in the City Hall, are among the matters of local importance which he specially promoted. He also took an active part in the management of the Andersonian University, the Glasgow Philosophical Society, Stirling's Library, and the Glasgow Humane Society. He was a Justice of the Peace for Lanarkshire, was one of the early directors of the Tharsis Copper Company, and was juror at the Exhibitions of 1851 and 1862. With such multifarious duties occupying his time, Mr. Harvey still managed to find leisure for the society of friends, and the pursuit of recreation, such as music and angling. The recent death of his distinguished younger brother, Sir George Harvey, President of the Royal Scottish Academy, and other severe family bereavements which happened not long before, greatly affected his already failing health, and his death occurred, not unexpectedly, on December 9th, 1876.

Jonathan Hearder was born at Plymouth, in 1809. He became an ardent student of science at a very early age, and although his father was greatly averse to his pursuits, he devoted all his spare time to experimental work, and to the contrivance of apparatus for illustrating lectures, of which, at the age of 17, he gave courses at the Exeter Literary Institution, and at other local societies. In 1830 he lost his sight by an accidental explosion while experimenting with silver-fulminate, but this calamity did not long interfere with his zealous pursuit of experimental science, especially electricity. In 1838 he succeeded to his father's business, and seven years afterwards was appointed consulting electrician and galvanist to the South Devon and East Cornwall Hospital. About September, 1846, sixteen years after

he lost his sight, he exhibited at the Cornwall Royal Polytechnic Society an arrangement of primary and secondary wires, with which sparks were obtained in air, and discharges several inches long, through rarefied air, and with which Leyden jars were charged. For this he received the silver medal of the Society. Ruhmkorff's induction coil was not made public until five years later, in 1851. An induction coil, constructed by himself, with a condenser which he also made himself, on principles which he had worked out, was exhibited by him in 1853-4, which gave with 4 cells of Groves's battery, better results than were obtained with the best instruments constructed by Ruhmkorff at that time. Hearder was also the inventor of a very useful magnetometer, with which he made a great number of experiments, with the object of ascertaining the rate of magnetic development in iron by successive additions of exciting elements of known power, applied through independent coils. He was intimately associated with Snow Harris, in many of his electrical researches, and devised numerous pieces of electrical apparatus, which, though somewhat rudely constructed by the blind experimenter, were of great ingenuity. He was one of the earliest to advocate the practicability of laying submarine telegraph cables of great length, and he invented a form of cable, a modification of which was ultimately used as a deep sea cable. Hearder was possessed of considerable chemical attainments, and was an eloquent lecturer, and a very successful experimenter before he was deprived of sight.

Although Hearder may have turned his knowledge of chemistry and his exceptional talents as electrician to some profitable account, his actual business to which he succeeded was that of maker of fishing tackle; but even in this direction there was room for the display of his ingenuity; he was, in fact, a specialist in the matter of fishing gear, and could prescribe the particular fly to be used for successful trout-fishing in any month, and for any stream in Devonshire. He was consulted about and designed the various fishing contrivances used by the "Challenger" Exploring Expedition. Hearder's life furnishes a remarkable illustration of the ardour and success, so far as the advancement of science is concerned, with which a true lover of science can contend against difficulties which by many would be counted insurmountable; and though he may have announced his connection with the Chemical Society in advertisements which included reference to his bread-winning employments, the Fellows of the Society will assuredly be none the less proud of that connection.

Francis Helvetius Hobler, the son of Francis Hobler, was born in Islington on the 24th July, 1838. His father was a solicitor, and his grandfather, who was of Swiss extraction, had been for fifty

years clerk to the Lord Mayor. He received the greater part of his education at the Boulogne College, where he attracted the esteem of his masters, and took a distinguished position. At this time, also, he manifested a decided propensity for scientific pursuits, chemistry and mechanics being the subjects to which he was most addicted. At the age of 16 he was articled in London to the legal profession, which he studied for five years, and, in due course, became entitled to practise. Hobler, however, had always felt that, though the principles of the law were great, the calling of a lawyer was very uncongenial to himself; indeed, his office-desk, instead of containing professional *matériel*, not unfrequently concealed the apparatus of a working electrical experiment. At length, he deserted a career which he found altogether repulsive, and entered, in 1860, as a student at the Royal College of Chemistry. At this institution, his progress was marked and rapid; and the few who, at that time, found admission within the circle of his modest reserve, discovered a keen and logical mind, eminently quick, suggestive, and full of resource. Here he remained until nearly the close of the session 1861-2, when he became one of the assistant chemists in the War Department Chemical Establishment at Woolwich, under the direction of Professor Abel. In carrying on the great variety of analytical and other experimental work which fell to Mr. Hobler's share in this establishment, he was continually striving to perfect existing methods and to devise new processes by which he might be more likely to attain the high standard of accuracy which was his constant aim. If he had a fault as an experimentalist, it was in the direction of a want of confidence in his own results. Mr. Hobler's services were of great value to Mr. Abel, and more especially so was his assistance in the complicated analytical investigation of the solid products of fired gunpowder, included in the researches of Messrs. Noble and Abel.

During the earlier portion of Hobler's career at Woolwich, his evenings were passed for the most part in the study of philosophy, literature, and languages; but he soon took a house, whither an affectionate aunt accompanied him, and he devoted one of its apartments to the purposes of a laboratory. His arrangements for efficient working in this somewhat confined space were ingenious and admirable.

It was natural that, sooner or later, Hobler should come in contact with the revelations, and investigate some of the problems, which the microscope presents to a scientific student. Among these, he was by none more attracted than by the movements designated "Brownian," wherein many inorganic and organic particles simulate the habits of the minuter living beings. A preliminary course of reason-

ing and experiment induced him to suppose that the movements in question were due to the agency of light. The verification of this hypothesis required an independent demonstration that light is capable of producing motion. He accordingly constructed a **I**-shaped iron box (which was exhibited to the Society), in which he suspended a very delicate, long-armed balance. On attempting to exhaust the box, he found that even a metallic casting is too porous to maintain a vacuum for a long time; but eventually this difficulty was overcome by a clever method of varnishing. The balance, standing in a vacuous space, gave a deflection when a candle-flame, or even the hand, was brought near one end of it. Hardly had this beautiful discovery been made, when Mr. Crookes read his first paper on the Radiometer before the Royal Society. Hobler immediately recognised and admitted that Crookes had anticipated him; but the most strenuous solicitations could not induce him to publish any account of his own quite independent research, and he could afterwards only be brought reluctantly to make any allusion to the subject. He seemed, indeed, to have an intrinsic dislike to publicity; and nothing of his work has been printed beyond a short paper on the electro-deposition of iron, communicated by Joule many years ago to the Manchester Literary and Philosophical Society.

Hobler's health had never been robust, though he was long unvisited by more than trivial ailments. In 1873, he suffered from a superficial complaint, from which he appeared to have satisfactorily recovered; but, unknown to himself, he was then attacked by diabetes. Ere long, he discovered the nature of the disorder that was evidently undermining him, and for which, as he soon learned, the physicians can only offer palliatives. Long and arduous was the inquiry he made into his own disease, whose symptoms it was, alas! his own interest to watch, and with the literature and expedients of which he became, unfortunately, too familiar. But every resource of others or himself proved in vain; and, drifting on without hope or chance, he gradually grew weaker, and expired painlessly on the 22nd November, 1876.

Hobler's temperament was somewhat melancholy, and he was reserved and sensitive. But those who knew him most intimately have much reason to regret his loss. To them he unwittingly betrayed a massive culture most unusual in a man of his years. French, German, and Italian he both spoke and read easily. Languages, indeed, were his favourite amusement; the earlier part of his illness was beguiled with Welsh and Hebrew,—the later, with the problems of the lost Etruscan. Of the modern school of philosophy and political economy, he would converse with the familiar tone of an experienced student. He had a refined musical taste, and was a good

amateur painter. No wonder that the few who were most near to him felt in a manner fascinated by such a mind, and could conceive for him an attachment deeper and more subtle than even friendship. They found him honourable and generous, and can remember his distinction between the great aims and the petty pastime of science. They saw him, dying in the shade, a patient critic, a deliberate student, of his own most hopeless misfortune.

Arthur S. Hobson was a scientific amateur. Unencumbered by business or professional cares, his attention was somewhat discursively given to a wide range of subjects; his favourite pursuits being, however, archæology, chemistry, and physics. He entered as a student at the Royal College of Chemistry in Oxford-street, about fifteen years ago, and studied there, for several years, under Hofmann and Frankland, and during this time he was elected a Fellow of this Society, and was always a frequent attendant at its meetings. He was also a member of the Physical, Meteorological, London and Middlesex Archæological, and Biblical Archæological Societies, and of the Royal Institution and the British Association for the Advancement of Science, at the meetings of which he regularly attended.

He died after a very short illness, almost suddenly, on October 24th, 1876, aged 61.

A large circle of personal friends will remember him as one whose integrity and kindness command their most sincere respect.

Charles Lambert was born in 1793. He received his education at the École Polytechnique in Paris, and, about the year 1812, took his degree as "Ingénieur des Mines." Not long afterwards, Mr. Lambert was appointed scientific attaché to a special mission sent by the French Government to Rio de Janeiro. On the return of this mission to France, he elected to remain behind, and afterwards made his way across the Andes to Chile, where he soon found a wide field for the practical application of his scientific knowledge.

Mr. Lambert may be called the founder of copper-smelting in Chile, a country which affords at the present time the largest amount of that metal, for although, before he established furnaces in Coquimbo, small quantities were produced by smelting the carbonates and oxides with charcoal in simple *ovens*, he introduced the reverberatory furnace, and at once utilised the enormous amount of sulphides, &c., which had hitherto been considered worthless. The exertions of Mr. Lambert in the metallurgy of Chile cannot be over-estimated, as he was the means of opening a multitude of mines in various districts of the Republic, which otherwise had been neglected. It may be added that Mr. Lambert, at the request of the Chilian Government,

induced M. Domeyko to undertake the professorship of Chemistry and Mineralogy in Santiago, to whom we are all so much indebted for our knowledge of the minerals in that interesting part of the world.

Mr. Lambert took an active interest in the progress of science, especially that of Chemistry, and in his will he provided that, under his son's direction, some funds should be devoted to the advancement of science.

Louis Arthur Lucas was the only surviving son of the late Mr. Philip Lucas, of Manchester, well known for his liberal charities in that town. He was born on September 23rd, 1851. He was educated at University College School, and afterwards studied at University College, where he showed a marked taste for experimental science. At an early age he evinced a decided inclination for a life of adventure, but he had to devote himself to mercantile pursuits. Before entering as partner in a house of business at Manchester, he proceeded to America, and after passing through Canada and part of the Eastern States, he made an excursion to Nebraska, where he hunted buffalo, and puzzled the Indian chiefs with tricks of jugglery at which he was very expert. The year after joining business, he was ordered to Egypt on account of bad health, and his return to England was delayed by an attack of typhoid fever, which rendered him an invalid for many months, during which time he devoted himself to the study of science. In 1875, he determined to devote himself to African exploration, his chief object being to seek out the sources and course of the River Congo. He left England in September, 1875, and arrived at Khartoum in January, 1876, where he remained for three months completing his preparations.

After considerable delay, he received permission of Colonel Gordon, the Governor of the Equatorial Provinces, to ascend the Nile into his district. Mr. Lucas reached Dardo in the month of June, and penetrated as far as the Albert Nyanza. It soon, however, became evident that his expedition could not succeed. His escort proved too weak and too untrustworthy for him to venture into the hostile country to the south. He therefore reluctantly retraced his steps northward, intending, however, on reaching Suez, to reorganise his expedition and then proceed, by way of Zanzibar, to the Lake Tanganika, and from thence prosecute his search of the sources of the Congo. That intention was never to be carried out. He was seized, on his return journey at Khartoum, by fever and dysentery, and after repeated attacks, became so prostrated that he was forced to abandon all further idea of African exploration. He then determined to return to England, and during an intermission of fever, on the

26th October started from Khartoum on his journey home. He reached Berber on the 2nd November, and Souakim on the 18th November, and then, in an exhausted state, he was put on board the s.s. "Massowah," bound for Suez. He died on board ship on the 20th November, at the early age of 25 years.

Maurice Lichtenstein, the son of Louis Lichtenstein, M.D., was born on the 15th of March, 1856. At an early age he showed a great predilection for study, and wished to follow his father's profession, but was compelled by ill health to relinquish the idea. He, however, devoted himself to scientific studies, and in 1873 he gained the Vintner Exhibition in Natural Science at King's College, Cambridge, also two scholarships at South Kensington.

In 1875 he was appointed an abstractor for the Journal of the Chemical Society, and in that capacity did good service in making abstracts of papers, chiefly relating to physiological chemistry, which was his favourite pursuit. His work was, however, carried on under a constant and painful struggle against a complication of maladies, to obtain relief from which he was advised at the beginning of last year to undertake a voyage to the West Indies. On this voyage he started, but he died four days after leaving England, on the 13th of February, in the 20th year of his age.

George Parry was born in 1813 at Ebbw Vale, near Newport, Monmouthshire, at which place and at the neighbouring town of Abergavenny, he received such an education as its schools afforded.

Leaving school at a comparatively early age, he commenced business with his father, a retail dealer in groceries, &c., a business for which he was eminently unfitted, and in which he took but little interest; indeed he was often censured for wasting his time in what appeared to his parents idle and profitless studies.

Even at this early age he manifested a special aptitude for the study of physics, and the whole of his spare time was passed in the construction of philosophical apparatus. During this period he acquired great mechanical skill, which, combined with considerable inventive power, later on became invaluable to him. The country at that time having no railway and but few roads, there were not many opportunities of communicating with the scientific world or with men of kindred tastes. Some idea may therefore be formed of the difficulties encountered and mastered by Parry in the pursuit of knowledge. In spite of these drawbacks he studied with success astronomy, geology, chemistry and the manufacture of iron, and he ultimately relinquished his more favourite study of astronomy and devoted himself entirely to the chemistry of iron manufacture, making analyses of the iron ores, coal,

&c., in the district, and holding consultations with the resident iron manufacturers, who soon learned to value and utilize his chemical and metallurgical knowledge.

About the time the hot blast was introduced; he rendered great assistance, and designed a hot blast stove, which is even now in use, and is considered by many as superior to some more recently designed.

Parry took a prominent part in utilizing the black-band ironstone, found in large quantities in the neighbourhood, making analyses and rendering considerable service in carrying out the smelting of this ore, which was at first attended with considerable difficulties.

In 1848 he obtained the appointment of metallurgical and consulting chemist at the Ebbw Vale iron works, and from that time until within a few years of his death, he applied himself solely to the metallurgy of iron, working unceasingly and ever alive to anything which bore upon the manufacture, or was calculated to lead to improvements in it.

He first directed his attention to the blast furnaces, and under his management plans for utilizing waste gases were designed, special attention being paid to the proper admixture of the gases with air to insure proper combustion. He also, in a series of papers written for the South Wales Institute of Engineers, showed that, in any given plane at right angles to the longitudinal axis of the furnace, it was necessary that the temperature should be uniform, otherwise the materials at the higher temperature would be reduced more rapidly than those at the lower; he prescribed the form of furnace most suitable and the other conditions necessary for the economical reduction of iron ore.

In 1854 the late Mr. J. Nasmyth proposed using steam for the more efficient purification of crude iron in the puddling furnace; this was tried at Ebbw Vale under Mr. Parry's superintendence, but ordinary steam could not be applied for any sufficient length of time, the iron cooling too rapidly. Mr. Parry tried superheated steam, heated by the waste heat of the furnace, with considerable success; the cooling action was much lessened, and the crude iron more effectually and rapidly puddled. Yet even superheated steam could only be applied to the puddling of grey iron, the ordinary white pig universally used in the district, even with superheated steam, cooling too rapidly; it was therefore, in combination with jets of air, used only for the refining of iron, producing a very superior refined metal, which was manufactured at the Ebbw Vale works until the use of refined metal was altogether given up.

About the year 1857 Mr. J. Martin proposed refining iron by passing air through the fluid metal whilst running down iron troughs, which were perforated with minute holes through which blast was

passed. Mr. Parry considered that the metal could not be thus refined to any extent, owing to the short time to which it was exposed to the blast of air, and proposed blowing the iron in a closed vessel, the bottom of which was perforated; this was done, and the iron became so hot that in a very short time the bottom melted down and the fluid contents of the furnace were lost.

It was noted that refined metal had been produced, also that the temperature, contrary to expectation, had increased, and the experiment would have been repeated, but in a few days the publication of Mr. Bessemer's paper, showing that iron could be blown in the way indicated and remain fluid, explained all and rendered further experiments unnecessary.

Seeing that Bessemer steel could be produced only from pure ores, of which there then seemed to be only a limited supply, Parry next directed his attention to the utilization of ordinary pig iron, observing that there was only one way of eliminating the excess of sulphur and phosphorus, viz., the puddling process. He thought that if the puddle-bar therefrom could be fused, it might be used for the manufacture of steel. Taught by previous experience, he thought that if, instead of blowing in the blast through horizontal tuyers, as practised in the ordinary cast-iron melting cupola, he *inclined* the tuyers so as to blow down on the red-hot puddle-bar, charged into the furnace with coke, sufficient heat might be generated to fuse the wrought iron.

The result far exceeded expectation. Not only was the wrought iron fused, but it took up about 2 per cent. of carbon; in fact, the fused product was simply a pure cast iron, which only required treatment by the Bessemer process for its conversion into steel.

This process was carried on with success at the Ebbw Vale works for some time, but ultimately it was found to be too costly, as compared with the Bessemer process, and the manufacture was therefore abandoned.

From 1857 to 1864 Parry was constantly occupied in carrying out his own processes, and in experimenting with the Bessemer process, which was then little understood. This work involved a vast amount of exertion, both mental and physical, under which his not very robust health gave way.

In 1866 he gave up his appointment and retired to Ferryside, a village near the sea in Carmarthenshire. Here he rallied for a short time, but it was evident that his constitution had been completely undermined; latterly, however, he suffered little, and died after only a short illness 6th February, 1877.

Mr. Parry was respected and esteemed very highly by the few who knew him intimately. His mind was always active, and to

the few who knew him he would confide from time to time the results of weeks' hard study and meditation, inspiring admiration by the originality and boldness of his conceptions.

He seemed to possess in a very unusual degree the faculty of concentrating his whole energies on the subject under consideration, to the total exclusion of everything else, and never rested until he had fairly exhausted the subject. To the possession of this faculty may be attributed his success in mastering the most difficult and abstruse subjects without assistance of any kind.

Alfred Smee was born on June the 18th, 1818, at Camberwell, and was the second son of William Smee, who for many years held the office of Accountant-General at the Bank of England. After a preliminary education at St. Paul's School, he devoted himself to medical studies, which he pursued first at King's College, and afterwards at St. Bartholomew's Hospital. In 1840 he was admitted a Member of the Royal College of Surgeons, and he became a Fellow in 1855. Mr. Smee occupied several important medical appointments. He was Surgeon to the Bank of England from the time of the creation of that appointment to his death. He was also Surgeon to the Royal General Dispensary, the Central London Ophthalmic Hospital, as well as to several other important institutions. He was, moreover, for some time Lecturer on Surgery at the Aldersgate School of Medicine, and among his numerous publications was a work on "Vision in Health and Disease."

Mr. Smee acquired at an early age a great love for chemical and electrical science, and important practical results were attained by him in the latter direction many years ago. In 1840 he constructed the form of voltaic battery known by his name, and in that year he received the gold medal of the Society of Arts, and was elected, at the age of 22, a Fellow of the Royal Society. He shortly afterwards published his well-known book on "Electro-metallurgy," and delivered lectures on this branch of applied electricity, with which his name has always been identified.

In 1854 he elaborated, in conjunction with the engineer and the printer of the Bank of England, the present form of Bank of England note, produced by the electrotpe process, and described it in a lecture to the Society of Arts "On the New Bank of England Note, and the Substitution of Surface Printing from Electrotypes for Copperplate Printing."

Mr. Smee published a large number of physiological and other works of considerable interest and importance, in addition to those on electricity and electro-metallurgy, which render his name more especially familiar to the chemist and electrician. His communication to

the Royal Society in 1843 on the cause of the reduction of metals from solutions of their salts by the voltaic circuit, and his paper of a still earlier date on the galvanic properties of the principal elementary bodies, may be referred to in illustration of his earlier contributions to electro-chemistry. Among his works of a more purely chemical nature may be mentioned his paper, published in 1840, "On Ferrosesquicyanuret of Potassium," communicated to the Royal Society, in which he pointed out, before Schönbein's discovery of ozone, that electrolytic oxygen converted the ferro- into the ferri-cyanide of potassium.

Of late years Mr. Smee devoted much of his leisure to the active pursuit of important branches of natural history, and laboured most successfully in the development of horticulture and pisciculture. The versatility of his genius was well illustrated by a work which he published under the title "My Garden," and by his activity as a Member of the Scientific Committee of the Horticultural Society.

As a man of great originality and breadth of views, and as one who pursued with indefatigable ardour, from pure love of enquiry, a very wide range of subjects connected with experimental and natural sciences, Alfred Smee commanded the admiration of his fellow-workers in science; while he was endeared to all those who had an opportunity of becoming acquainted with his enthusiastic love of nature and his frank and genial disposition. He died on 11th January, 1877.

Thomas Heathcote Gerald Wyndham was born 11th October, 1842. Having received his preliminary education from the Rev. J. Addison, at Weymouth, he passed five years at Eton, and at the age of 19 matriculated at Oriel College, Oxford. In 1865 he took a first-class degree in Natural Science. In 1867 he was elected to the Burdett-Coutts Geological Scholarship, and in the same year he was elected to a Natural Science Fellowship at Merton College. Mr. Wyndham devoted himself ardently to study and development of petrology, and he has bequeathed his scientific instruments, books, and collection of rocks and minerals in trust for the use of the first university which shall create a Professorship or Readership of Petrology. Mr. Wyndham died in November, 1876. He was eminent at Oxford for his devotion to, and diligence in the work of teaching, and was conscientious, even to over-sensitiveness, in looking to the instruction and necessities of his pupils. Being an earnest advocate of reform at the University, it often became his duty to espouse the cause of measures which were distasteful to many of his intimate associates and colleagues. But his invariable courtesy to and respect for the feelings of opponents in controversy was as remarkable as his conscientiousness for his allies in any joint enterprise. Had he lived, he

might have earned and obtained a permanent public reputation. As it has unhappily fallen out, the memory of him will be limited by the extensive circle of his attached personal friends.

Dr. Frank Smith was born at Nottingham, about 1836, and was educated at Bromsgrove Grammar School, Worcestershire. After some hesitation between Oxford and the Church, on the one hand, and his father's mercantile pursuits on the other, he decided to follow the medical profession, and was articled to the late Mr. Ewen, of Sutton. In 1858 Mr. Smith commenced his studies at Guy's Hospital, and soon devoted special energy to the pursuit of chemical science, which he studied under Dr. Odling. He was a constant attendant and a frequent and brilliant speaker at the Guy's Physical Society, and was unremitting in his earnest devotion to his studies, and to the duties in connection with the hospital which devolved upon him. After completing his course of study in London, he proceeded to Dublin in 1862, where he worked for some months, chiefly at obstetric medicine, and he afterwards studied for several months in Professor Wurtz's Laboratory, at Paris. In 1863 he unsuccessfully contested the appointment of Demonstrator of Chemistry in Guy's Hospital School, and then pursued his medical studies for some months further at Edinburgh. Having taken his degree at the University of London, in 1864, he was appointed Physician to the Sheffield Public Hospital, and devoted himself chiefly to his hospital practice and his lectures at the Medical School, though he occasionally found time to pursue microscopic and spectroscopic studies. He subsequently was appointed to the Infirmary, and had established a rapidly increasing practice as consulting physician, when his health suddenly gave way, in 1875, and after an alarming seizure, it soon became evident that he was suffering from Bright's disease. Dr. Smith left Sheffield at the end of that year, and settled in Devonshire, where for about twelve months he enjoyed comparatively good health, and devoted himself chiefly to his favourite literary pursuits and electrical experiments. He had even re-commenced practice at Torquay, but on the 10th of January he was suddenly attacked, while walking with his wife, by the same alarming symptoms which had seized him when his malady had first developed, and died after an illness of six days.

Dr. Smith was a good general scholar, and ardently fond of poetry. He published a volume of his own poems in 1864, which met with some success. He was also the author of several papers on medicine and the allied sciences. He possessed in a high degree two of the chief qualifications of a physician, acuteness and sympathy, and was greatly beloved and respected, both in his professional capacity and for his personal worth.

Antoine Jérôme Balard was born at Montpellier the 30th September, 1802, of humble parents, vine-growers, who cultivated their own small domain. Their son remained with them during his infancy, and was afterwards adopted by his godmother, who charged herself with his education. After successful studies at the College of Montpellier, he became, at the age of 17, Préparateur at the Ecole de Pharmacie, where he received his diploma in 1826. At that time he devoted himself to chemistry and botany, and later on he studied and taught physics. His mind showed an aptitude for all branches of science, and he soon furnished a striking illustration of his penetration and his experimental talents.

About 1824, while botanising near a salt marsh, he had observed a deposit of sodium sulphate which, during a cold night, had crystallised in a pan containing the mother-liquor from common salt. The idea of utilising these mother-liquors immediately occurred to him, and occupied his mind during the greater part of his life. In the course of his experiments he was struck with a peculiar coloration, which certain reagents produced in these liquors. Pursuing this track with the energy peculiar to inventive genius, he had the good fortune to discover bromine—an elementary body which, unlike those rare metals which lay hidden in obscure minerals, assumed a position of importance as ranking with chlorine, discovered by Scheele, and iodine, for the discovery of which we are indebted to Gay-Lussac. Thus the name of the young chemist of 24 years of age became associated with those of these illustrious men.

Attention was immediately directed to this new body; its properties and principal compounds were studied by Balard, and described in a classical memoir. Gay-Lussac congratulated the young chemist, and exhibited the new element in his lectures, and the Royal Society awarded him its highest distinction. At Montpellier the reputation he thus acquired was soon of material aid to him. He was appointed successively to the School of Pharmacy, the Collège Royal, and, in 1834, to the Faculty of Sciences. He thus attained a position which afforded him not only means of subsistence, but also the means of pursuing experimental work. But the straitened circumstances of his early life exerted a marked influence over his mode of work. His habits of economy and desire to provide for the future wants of his family led him to avoid outlay, and to give the preference in his experimental work to simple processes and primitive apparatus. His reagents were prepared by himself, and he delighted to recall the great discoveries which emanated from Scheele's humble resources. He could not have selected a better example, though it must be submitted, on the other hand, that if simplicity of methods of expe-

riment is an advantage from the point of view of economy, it is not always compatible with the precision which should be arrived at in all experiments. Balard's experiments have, however, always possessed that precision, and his discoveries have never been contested, while they bear the stamp of his great originality of mind. Thus, those of hypochlorous acid and oxamic acid filled up important gaps and opened up new views and fields of experiment.

He was engaged in the study of the oil which separates on the distillation of "eau de vie de Marc," namely, amylic alcohol, when he was called to the chair which had been occupied by Thénard at the Faculté des Sciences in Paris, at the time when Dumas filled the chair before occupied by Gay-Lussac. His vivacity of language and lucid exposition commanded the attention of an auditory difficult to please. Later on he carried on with equal success and distinction his instruction at the Collège de France, where he succeeded Pélouze in 1850.

Balard lived in Paris 38 years, and this period was, if not the most productive, at any rate the most useful of his life. He was elected to the Académie Française in 1844. From that time he took the most lively interest in the progress of science. With regard to his own labours, he devoted himself more to the development of his earlier discoveries than to the prosecution of new ones. In 1840 he had patented a method of extracting potassium salts from the mother-liquors of salt marshes, from which sodium sulphate had already been separated. His laboratory experiments determined the conditions to be fulfilled in the separation of these salts, and for 40 years he pursued the application of his researches to industrial purposes; but though his perseverance was crowned with success, that success was, as often is the case, not so complete from a material point of view as might have been wished. Just when the last difficulties had been overcome, the almost inexhaustible deposits of potassium salts near Stassfurt were discovered, nature having achieved on a large scale that which Balard had succeeded in accomplishing. With regard to the discovery of bromine, Balard had also to content himself with the conviction that his discovery had benefited mankind. Balard was of a happy temperament, but was well acquainted with adversity. His three children were removed by death, and he survived his wife, whose children by a former marriage he had adopted, and who have been a comfort to him in his declining years. Though his circumstances improved in late years, he continued to lead a plain and almost ascetic life, while indulgent and liberal to others; and, while he denied himself simple enjoyments, he was ever ready to succour those who appealed to his bounty. His upright character, thorough goodness, and modesty, combined with great warmth of

heart and generosity, made him beloved and revered by all his associates.

The Society has again to be congratulated upon an increase in the number of original communications which have been received during the past year, and upon the high order, in point of interest and importance, of a large proportion of these. Last year 66 papers were communicated to the Society; this year the number is 71, and the following are their titles:—

- I. "Preliminary Notice on the Action of Sulphuric Acid on Naphthalene:" by Dr. Stenhouse and C. Groves.
- II. "On the Action of the Copper Zinc couple on Potassium Chlorate and Perchlorate:" by H. Eccles.
- III. "On Thallium Chlorate:" by J. Muir.
- IV. "On the Isometric Relations of Thallium:" by E. T. Thorpe.
- V. "On Systematic Nomenclature:" by Dr. H. E. Armstrong.
- VI. "On the Manufacture of Sulphuric Anhydride:" by Dr. Messel and Dr. Squire.
- VII. "On Glycerophosphoric Acid and its Salts as obtained from the Phosphorized Constituents of the Brain:" by Dr. Thudichum and C. T. Kingzett.
- VIII. "On some Reactions of Beliverdin:" by Dr. Thudichum.
- IX. "On the relation between Chemical Constitution and Colouring Power of Aromatic Substances:" by Dr. Otto Witt.
- X. "On Certain Bismuth Compounds, Part II:" by M. M. P. Muir.
- XI. "A new Method for preparing the Hydrocarbons Diphenyl, and Isodinaphyl, and on the action at a high temperature of Metallic Chlorides on certain Hydrocarbons:" by Watson Smith.
- XII. "On the Action of Water and various Saline Solutions on Copper:" by T. Carnelley.
- XIII. "Notes on some Experiments made with a view to ascertain the practical value of a Proposed Method of determining the Mineral Strength of Soils by means of Water Culture:" by G. A. Hight.
- XIV. "On the Action of Malt Extract on Starch:" by C. O. Sullivan.
- XV. "On Metaxenol:" by Dr. H. E. Armstrong and Mr. Gaskell.
- XVI. "On Gases enclosed in Cannel Coal and in Jet:" by J. W. Thomas.
- XVII. "On Phenomena accompanying the Electrolysis of Water with

- Oxidizable Electrodes:" by Dr. J. H. Gladstone and A. Tribe.
- XXVIII. "On the Estimation of Hydrogen occluded by Copper, with Special Reference to Organic Analysis:" by Dr. Thudichum and H. W. Hake.
- XIX. "On Hemin, Hematin, and a phosphorized Substance contained in Blood-corpuscles:" by Dr. Thudichum and C. T. Kingzett.
- XX. "On Natural Carbon Dioxide from various Sources:" by W. N. Hartley.
- XXI. "On some trials of Frankland and Armstrong's Combustion-process *in vacuo*:" by Dr. Thudichum and C. T. Kingzett.
- XXII. "On Peroxides; on Chromic and Perchromic Acids; and on the Estimation of Nitrogen:" by T. Fairley.
- XXIII. "On Aluminium Nitride and the Action of Aluminium on Sodium Carbonate at High Temperatures:" by J. W. Mallet.
- XXIV. "On the Volumetric Estimation of Mercury:" by R. V. Tuson and E. Neison.
- XXV. "Chemical Studies:" by P. Dewar.
- XXVI. "Researches on the Reduction of Nitric Acid and on the Oxides of Nitrogen, Part I; on the Gases Evolved by the Action of Metals on Nitric Acid:" by Mr. Ackworth and Dr. Armstrong.
- XXVII. "On an Alkaloid obtained from Jaborandi, its Platinic Compound, and their Formulæ:" by C. T. Kingzett.
- XXVIII. "The Simultaneous Action of Iodine and Aluminium on Ether and Compound Ethers:" by Dr. Gladstone and A. Tribe.
- XXIX. "On some Compounds of Antimony Pentachloride with Alcohol and with Ether:" by W. C. Williams.
- XXX. "On the Volatility of Barium, Strontium, and Calcium:" by J. W. Mallet.
- XXXI. "On the Action of Chlorine on Acetamide:" by E. W. Prévost.
- XXXII. "Note on the Perbromates:" by M. M. P. Muir.
- XXXIII. "On a New and Convenient Form of Ureometer:" by Dr. J. G. Blackley.
- XXXIV. "On the Oxides of Potassium:" by Sidney Lupton.
- XXXV. "On certain Bismuth Compounds:" by M. M. P. Muir.
- XXXVI. "On Phospho- and Arsenio-cyanogen:" by W. R. Hodgkinson.
- XXXVII. "A Secondary Oxidized Product formed during the

- reduction of Stannic Ethide:" by W. R. Hodgkinson and G. C. Matthews.
- XXXVIII. "A Preliminary Notice on *Pigmentum nigrum*, the Black Colouring Matter contained in Hair and Feathers:" W. R. Hodgkinson and H. C. Sorby.
- XXXIX. "On Barwood:" by the late Dr. Anderson.
- XL. "The Alkaloids of the Aconites, Part I; on the Crystallisable Alkaloids contained in *Aconitum Napellus*:" by Dr. C. B. A. Wright.
- XLI. "On Potassium Triiodide:" by G. S. Johnson.
- XLII. "On the Coal Gas of the Metropolis:" by T. S. D. Humphidge.
- XLIII. "On Colein:" by A. H. Church.
- XLIV. "On Phenylenediamine:" by Dr. Otto Witt.
- XLV. "On Calcium Sulphate:" by J. B. Hannay.
- XLVI. "Additional Notes on Potassium Triiodide:" by G. S. Johnson.
- XLVII. "A further Study of Fluid Cavities:" by W. N. Hartley.
- XLVIII. "On Thymoquinone:" by Dr. H. E. Armstrong.
- XLIX. "On High Melting Points, with special reference to those of Metallic Salts, Part II:" by T. Carnelley.
- L. "On the Estimation of Urea:" by G. Turner.
- LI. "On the Corrosion of Lead by the New River Company's Water:" by G. Bischof
- LII. "On some Derivatives of Dithymyltrichlorethane:" by Dr. Jäger.
- LIII. "Preliminary Account of some Reactions in Organic Chemistry and their ultimate bearings:" by H. W. Hake and C. T. Kingzett.
- LIV. "On Dinitroso-orcein and Dinitro-orcein:" by Dr. J. Stenhouse and C. E. Groves.
- LV. "On High Melting Points, with special reference to those of Metallic Salts, Part III:" by T. Carnelley.
- LVI. "On Kekulé's and Ladenburg's Benzene Symbols:" by Dr. H. E. Armstrong.
- LVII. "On the Formation of Coumarin and of Cinnamic and other analogous Acids from the Aromatic Aldehydes:" by W. H. Perkin.
- LVIII. "On the Estimation of Urea by means of Hypobromite:" by Dr. Dupré.
- LIX. "On a new Carbometer for the Estimation of Carbonic Anhydride:" by S. T. Pruen and G. Jones.
- LX. "On the Influence Exerted by Ammonium Sulphide in pre-

- venting the Action of various Solutions on Copper:" by F. W. Shaw and T. Carnelley.
- LXI. "An Experimental Enquiry as to the Changes which occur in the Composition of Water from Wells near the Sea:" by W. Watson.
- LXII. "On the Solvent Action of various Saline Solutions on Lead:" by M. M. P. Muir.
- LXIII. "Derivatives of Di-isobutyl:" by W. Carleton Williams.
- LXIV. "Notes on Madder-colouring Matters:" by D. Schunck and H. Roemer.
- LXV. "Additional Note on a Method of Estimating Bismuth volumetrically:" by M. M. P. Muir.
- LXVI. "Note on Gardenin:" by Dr. Stenhouse and C. E. Groves.
- LXVII. "Preparation of Copper-Zinc Couples:" by Dr. Gladstone and A. Tribe.
- LXVIII. "On Chromium Pig Iron:" by E. Riley.
- LXIX. "On Isomeric Nitrosoterpenes:" by Dr. Tilden.
- LXX. "On certain Bismuth Compounds, Part IV:" by M. M. P. Muir.
- LXXI. "The Determination of Urea by means of Hypobromite:" by D. M. Simpson and C. O'Keefe.

Two discourses of very special interest and value have been delivered to the Fellows during the past year. In the one, by Prof. Andrews, "On certain Methods of Physico-chemical Research," a masterly description was given of the admirably simple and efficient appliances and methods of experiment employed by the lecturer in the beautiful and important researches which have immortalised his name; in the other, "On the Theory of the Bunsen Flame," Prof. Thorpe gave a lucid and happily-illustrated account of recent interesting investigations into this subject and into the causes of the luminosity of flame. Arrangements have been made for the delivery this session of an experimentally-illustrated lecture by Prof. Maskelyne on the discrimination of crystals by their optical characters, and the Fellows are to be congratulated on the successful commencement which has been made in applying experimental illustration to the enhancement of the interest and value of discourses and original communications."

In last year's Report reference was made to the very satisfactory circumstance that, for several years previously, the income of the Society had pretty steadily increased at the rate of about £100 annually, while the balance-sheet of that year showed a very much greater

increase, which, though it was to some extent due to exceptional causes, arose in part from an addition to the number of Fellows considerably above the recent average proportion.

On the present occasion it is the duty of the Council to report in less favourable terms of the financial progress of the Society. The Fellows were prepared by last year's statements to learn that the income of the Society would have to bear a greatly increased burden in the year now closing. The source of extra income arising from special subscriptions of Fellows to the publication fund, amounting to about £250, which had been guaranteed for five years, and from the annual grant of £100 for the same term from the British Association, has ceased, and the entire cost of publication of the Journal has consequently been borne this year by the ordinary income of the Society. This cost has at the same time been very considerably increased, as was anticipated, by the permanent increase in the size of the Journal, and the consequent publication of two volumes in the year in place of one. The Council estimated this increased expenditure in connection with the Journal at about £300; it has actually amounted to about £239, the greatest care having been taken to reduce the cost of printing the Journal to a minimum.

The measures adopted, on the recommendation of the Council, with the view of partly meeting the considerably increased demand upon the Society's income, were: an increase in the selling price of the Journal; the increase of the admission fee paid by newly-elected Fellows from £2 to £4, and the discontinuance of the purchase of the Proceedings of the Royal Society for the Fellows. The saving which will result from the last-named measure (about £120) will not take effect until the commencement of the Society's new financial year; the other two sources of profit have together furnished this year about £144 towards defraying the increase of expenditure of about £590, which has to be borne by the Society's funds.

In estimating the future resources of the Society in the shape of regular income—a matter which received the most careful consideration of the Council before they decided to increase the expenditure upon the Journal, they considered themselves fully warranted in anticipating that the average annual increment arising from an increase in the numerical strength of the Society would at any rate not fall short of that of the last few years. The Council regret to have to report that an action on the part of some few of the Fellows has, for this year, prevented the realisation of that well-grounded anticipation.

The actual addition to the numerical strength of the Society this year is not only considerably less than half that of last year, but is also less by about two-fifths than the mean increase of the three previous years. The following numbers are instructive on this point:—

	Number elected.	Actual addition to Number of Fellows.
1870-1	41	29
71-2	42	31
72-3	59	42
73-4	70	58
74-5	76	51
75-6	103	80
76-7	65	35

They show that, in the matter of addition to the Society's income, arising out of an increase in its numbers, instead of a continuance of the progressive rate of increase, maintained with one trifling exception, during the previous five years, we have this year reverted to about the rate which had been attained five years ago.

There is little doubt that this very serious falling off in the rate of addition to the numerical strength of the Society is to be ascribed, not only to the number of candidates black-balled (20 per cent. of the total number proposed in the year), but also to the effect which certain instances of palpably unjust exclusion from the Society have had in deterring candidates, possessed of unquestionable qualifications, from offering themselves for election, and in rendering old Fellows of the Society of high standing as chemists, reluctant to submit to a disregard, by a small section of the Fellows, of their vouchers of the eligibleness of candidates proposed by them.

The black-balling of candidates had, at the commencement of the Society's new year, already developed into what could not be otherwise regarded by those officers of the Society who, in the performance of their duties connected with the ballots became acquainted with its operation, as an organised system, perseveringly pursued, with no very great regard to discrimination, by a small number of those Fellows of the Society who regularly attend the meetings. The rejection of more than one candidate possessing claims for admission to the Society at least equal to those of a very large proportion of its Fellows, afforded evidence that the future welfare of the Society was becoming most seriously imperilled. It therefore became the duty of your President to direct the attention of the Council to the subject, and, at their request, to point out to the Fellows at one of the ordinary meetings the grave character of the results, as affecting the interests and the fulfilment of the real objects of the Society which must accrue from a perseverance in the somewhat sweeping system of black-balling pursued.

Unquestionably, as shown by the correspondence in a scientific periodical, which followed upon the observations offered by me, with

the approval of the Council, those Fellows who have liberally exercised their undoubted right to vote against gentlemen recommended as eligible for admission by other Fellows of the Society, did so, in the first instance at any rate, from a desire to promote, from their own particular point of view, the interests of the Society and the advantages to be derived from belonging to it. Unquestionably also, it would not have injuriously affected the prosperity of the Society—though it may be open to question whether its status would have been different from what it now is, if the right of black-balling had in years past been somewhat more frequently exercised by the Fellows than has been the case with the exception of one brief period in the Society's history, when the recurrence at several successive meetings of instances of unreasonable black-balling led the Council to appoint a Committee to consider and advise upon the mode of election of Fellows. The Report presented by that Committee bears so thoroughly upon the arguments which have been publicly put forward by the advocates of the system of black-balling recently pursued, that it merits careful perusal by the Fellows, and is therefore appended to this Report. It should be stated that the Committee did not recommend any alteration in the mode of election of Fellows.

With regard to the action which has been taken recently by some of the Fellows in the matter of election of candidates, it is right that the following facts should be placed before the Society:—

1. The largest number of negative votes which has been recorded in the recent cases of black-balling is eight or nine, or about one-hundredth part of the total number of Fellows; but as a number of negative votes one-fourth the total number voting excludes a candidate, less than the above number suffices to ensure the black-balling of a candidate unless there is an exceptionally numerous attendance of Fellows at the commencement of the meeting.

2. It has frequently happened of late that a large proportion, if not the majority, of the candidates put up for ballot on one evening, has received the same number of black balls; at the same time, it need hardly be stated that the nature and amount of qualification of such candidates and the number and class of names attached to the certificates were very different.

3. The exclusion of candidates has not only been applied to gentlemen of good social position and scientific tastes desirous of improving their knowledge by attending the Society's meetings and associating with its Fellows; it has also and chiefly been applied to particular classes. Thus a candidate, however eligible in point of scientific attainments, need only to have been described as Science Teacher, to ensure his exclusion.

The necessity for exercising careful discrimination in the election of

Fellows has been demonstrated by reference to a few cases in which men of questionable qualifications have in past years been elected, and of a very small proportion of cases in which improper use has been made for advertising purposes of the title F.C.S. by persons who have either obviously sought admission into the Society purely for trade purposes, or who have subsequently considered it advantageous and not improper to attempt to reap benefit from their connection with the Society.

It is obviously difficult to assign a precise limit to what may be considered a legitimate use, for professional or trade purposes, of the title assumed by members of a Society founded for the cultivation of a particular science, especially when it never was contemplated by the founders of a Society of this kind that such a title should constitute a proof of, or voucher for, the possession of particular degrees of qualification by its members. As, however, the public has been educated by scientific men, especially by men practising in the application of a science as means of livelihood, to regard such titles as affording some guarantee of qualification, it must be admitted to be a hardship to men of undoubted position in a science, such as that of chemistry, who have had up to the present time no other means of indicating their qualification, as professional men, to the public than by the use of such a title, to find its value degraded by its occasional employment for purposes quite distinct from professional. Hence it cannot be denied that there have been very reasonable grounds for endeavouring to exclude undesirable candidates for admission into the Society by an exercise of *greater* discrimination at ballots, and by some increase in the stringency of the terms under which a person has to seek admission into the Society.

Your Council, giving full weight to these considerations, devoted their earnest attention soon after the last anniversary meeting to the subject of the admission of Fellows. They might perhaps have received valuable aid in their consideration of the subject, had they been favoured by some statement of the views of that section of the Society which must be considered to have given expression, by the perseverance in systematic black-balling, to dissatisfaction of some kind with the existing arrangements or practices. No steps were, however, taken to inform the Council of the real cause for dissatisfaction, or of any views more or less prevalent with regard to its possible remedy. After careful discussion, it was decided to modify the form of proposal of a candidate, in order to insure that a full and detailed statement of his qualifications is furnished by the Fellows who sign his certificate. The Council also decided to recommend to the Fellows a slight modification in the wording of the obligation which is signed by newly-elected Fellows upon their admission, with the view of

making it somewhat more precise and binding, and have resolved that this obligation shall be read aloud by the Secretary to the Fellows before signing the admission-book, in order that they may not plead ignorance of the terms under which they are admitted to the Society, while the Fellows attending the meetings may be at the same time reminded of their pledge to support the interests and dignity of the Society.

It was to be hoped that this black-balling which continued to be persevered in by a few Fellows of the Society, as above indicated, would have become reduced in extent to the limits prescribed by a just consideration of the claims of individuals, as vouched for by Fellows thoroughly competent to do so; in the first place, in consequence of the action taken by the Council to increase the stringency of the election as far as can be reasonably done in view of the real functions of the Society; secondly, and more especially, in consequence of the establishment of a purely professional Society or Institute, which will secure to practising members of the chemical profession the status and the desirable distinction, in the eye of the public, from amateurs or persons whose qualifications may, on some point or other, be open to question, which could never have been attained by attempts to exclude particular classes from admission to the Society. The results of even the most recent ballots have, however, demonstrated that indiscriminate black-balling (*i.e.*, the exclusion of classes without reference to the qualifications of individuals included in such classes) is still the course which recommends itself to some Fellows as conducive to the carrying out of their personal views; it may perhaps be hoped that the very injurious manner in which their action is affecting the Society's future prosperity will receive from them that serious consideration which it is time it should receive at the hands of the general body of Fellows.

At a meeting of Professional Chemists, held by permission of the Council in this room last April, a Committee was appointed to confer with the Council of the Chemical Society, with the view of ascertaining whether a scheme for organising the profession of practising chemists could be carried out by the Chemical Society in conformity with the terms of its Charter. A scheme submitted by this Committee, to confer with which the Council in the first instance appointed a small committee from its own body, received the most careful consideration of the Council, who agreed unanimously to a series of propositions based upon this scheme, and embracing all the points included therein which it was possible to do without departing from the laws governing the Society as laid down by its Charter. These propositions, which they would have been prepared to submit to a general meeting of the Society, met the views of the Committee of Chemists, except in one point which

was considered by them of vital importance, and which after serious re-consideration of the subject and consultation with eminent legal advisers, the Council decided that it was impossible to meet unless the terms of the Charter could be modified. The negotiations were consequently closed by the receipt of a communication from the Chemists' Organisation Committee, thanking the President, Officers, and Council for the cordiality with which they had endeavoured to institute a scheme for the organisation of Chemists within the Society, and regretting that, after mature deliberation, the obstacles in the way of carrying out the wishes of the promoters of the Organisation Scheme appeared so formidable as to render it undesirable to prosecute the attempt further. It is doubtless within the knowledge of most Fellows of the Society, that a scheme for the formation of an independent Institute of professional chemists has recently been matured—an Institute which will, it is believed, embrace a large section of the Fellows of this Society, and will, it is hoped, secure to practising chemists the distinctive position and recognised status which they justly desire, while its members will labour in harmony with the Chemical Society for the advancement of science.

While the subject of the qualifications of candidates for Fellowship was under the Council's consideration, the advisability of rendering the grade of Associateship, which is provided for in the Society's Charter, more important than it has hitherto been, was carefully discussed.

According to the present bye-law of the Society relating to Associates, they are elected by the Fellows, on the recommendation of the Council, for a period of three years, subject to re-election. They pay no subscription, and their privileges are limited to admission to the ordinary meetings and to the library. Hitherto the applications for admission as Associates have been extremely limited; this may be ascribable in part to the limited nature of the privileges which that grade offers; in part to the very fact of its not entailing the payment of a subscription. It was suggested to the Council that, if greater prominence were given to the grade of Associate, it might be regarded by young men who are devoting themselves to the study of chemistry, as a stepping-stone to the Fellowship of the Society, and would certainly be useful to them by placing within their reach the resources of a chemical library, which year by year is progressing towards completeness. The grade of associateship might also present a desirable opening for admission to the Society, to others whose qualifications might not be of a nature to ensure their admission, at any rate in the first instance, as Fellows. The Council, adopting these views, resolved to recommend to the Fellows an alteration of the bye-law relating to Associates, to the effect that they should have the privileges of admis-

sion to the ordinary meetings, and the full use of the library, on the payment of an annual subscription of £1, and that an additional payment of 10s. annually should entitle them to the Society's Journal, which they would thus obtain at a lower rate than that at which it is supplied to the public. The Council submit that the adoption by the Fellows of this alteration of the bye-laws, added to the modification which they have made in the form of proposal of a candidate for Fellowship, will meet every reasonable proposal which has suggested itself in reference to modifications in the matter of elections into the Society.

The Council have to report that the Dircks legacy, referred to in the last annual report, and amounting to between £700 and £800, has been received by the treasurer, and has been invested in London and North Western Debenture Stock. The question whether the proceeds of this investment shall be devoted to any one special work of the Society will be for the consideration of your new Council.

Subscriptions to the amount of £1,000, the minimum sum required to fulfil the stipulation under which Dr. Longstaff offered to make a donation of that amount to the Society, for the purpose of establishing a fund for promoting the advancement of chemical science, were received some months since, and indeed that amount has now been a little exceeded by the donations made to the fund by Fellows of the Society. The Council having observed, however, that the subscribers to the fund included but a small number of gentlemen who are or have been prominently connected with chemical industries, and from whom they had anticipated that Dr. Longstaff's proposal would have received liberal support, it was decided to direct the attention of chemical manufacturers once more and specially to the subject, in the belief that the first appeal made by circular had not placed its importance before them with sufficient prominence or force. A second circular has therefore been quite recently issued, and some responses already received to it encourage the Council to hope that this renewed appeal will bear good fruit.

From another, at first quite unlooked for direction, the fund has received most important additions. It occurred to your President and Treasurer to suggest to Mr. Bramwell, F.R.S., the eminent engineer, one of the wardens of the Goldsmiths' Company (a Company which has on several occasions of late afforded practical proof of its desire to aid in the advancement of science and its application), that a suggestion to aid in the fulfilment of Dr. Longstaff's proposal might perhaps receive favourable consideration from the Company. Mr. Bramwell at once joined an old Fellow of this Society, Mr. George Matthey, who was recently a warden of the Company, in warmly espousing the

Society's cause, and with such signal success that, on the motion of Mr. Matthey, the munificent sum of £1,000 was voted by the Wardens and Court of the Goldsmiths' Company, as a contribution to the Society's Research Fund, the vote being unfettered by any conditions whatever as to the application of the money. Encouraged by this success, your President has memorialised several other of the wealthier City Companies, to influential members of which he has obtained access. The result, so far, has been the receipt of one hundred guineas from the Merchant Taylors' Company, and of a similar sum from the Clothworkers' Company, and there is good reason for hoping that donations will be received from two or three other Companies.

Dr. Longstaff's contribution to the fund, invested in North British Preference Stock, was transferred by him to the Society a short time since. Your Treasurer has, in addition, invested £2,000 in Metropolitan Stock, and it may be hoped that a further substantial investment will ere long be made. The Council whom you will presently elect will have the important duty of considering what recommendations shall be submitted to the Fellows with regard to the application of the proceeds of this valuable accession to the Society's resources.

Dr. Longstaff, in placing his donation in the Society's hands, has made two stipulations, viz., 1st. "That a sum of not less than £2,000 be funded, the proceeds only of that fund being devoted to the object in view;" and 2nd. "That a gold medal of not less value than £20 be awarded, triennially, to the Fellow of the Society who, in the opinion of the Council, has done the most to promote Chemical Science by Research." Your Council feel sure that they have but anticipated the unanimous wishes of the Fellows of the Society in presenting to Dr. Longstaff a formal record, suitably engrossed, of the Society's gratitude to him for his munificent donation, through the instrumentality of which an important extension of its sphere of usefulness promises to be secured.

In concluding this Report in which, as Chairman of the Council, I have been its spokesman, I have to state that I take upon myself the entire responsibility of all it may contain which is beyond the limits of a simple statement of facts. When you were pleased to consider me worthy of being placed in the proud position of President of this Society, in whose interests I have laboured arduously for a number of years, and whose welfare I have therefore most warmly at heart, I could not but doubt my worthiness to occupy a Chair which has been filled by men universally esteemed as among the most illustrious cultivators of Chemical Science, being painfully alive to the fact that my official career has debarred me from being, as your President, a worthy representative of pure science, which it is the chief aim of this Society to advance. But, having been entrusted by you with this most honourable and responsi-

ble office, I have striven to my utmost to uphold the dignity and advance the activity and prosperity of the Society, and if, in thus striving, and not shrinking from any step which, after careful consideration, I have regarded as a duty I owe to the Society, I have been considered by any one of its Fellows to have used at all too freely the privilege of outspokenness, which a President may claim in the fulfilment of his duties, I trust that honesty of purpose and zeal for the Society's welfare will be admitted as valid excuse. In relinquishing the office of President, I must express my gratitude to the Fellows for the indulgence they have extended to me, and to my colleagues, the officers of the Society, for the invaluable aid they have afforded me, by the zealous and most efficient manner in which they conduct the by no means trivial duties connected with the management of its affairs.

The Treasurer then read his Report, Messrs. Carteighe, Friswell and Nicholson being auditors.

Mr. E. Neison said he would like to draw the attention of the Fellows to two or three matters, before the adoption of the President's Report was moved, and then pointed out (1) that, although the general index to the Society's Journal had cost a large sum, £282, comparatively few copies had been sold; he thought it would be advisable to distribute the index gratuitously to the Fellows; (2) that the laboratory was very insufficiently supplied with apparatus and chemicals; he suggested that when the Society granted money to chemists for assisting them in conducting original research, they might at the same time place the laboratory at their disposal; (3) that a very long time, three or four months or more, elapses between the reading of a paper at one of the Society's meetings and its appearance in the Journal. He concluded with some remarks on the black-balling which has recently taken place in the Society.

Professor Williamson remarked that it was most important that some appropriate occasion should be offered for the discussion of various matters affecting the welfare of the Society, and was very glad that they now had an opportunity of talking over this matter of the black-balling together. He was very jealous of the privilege or rather duty of the Fellows of excluding those candidates who were not properly qualified, but at the same time this function should be exercised with the greatest discretion. No doubt this action had been taken on some principle, but it was a principle which he did not understand; and if, instead of producing the effect they desired, it had produced others of an unexpected and perhaps disastrous character, he hoped those members who had exercised this privilege would reconsider their mode of action, which, if continued, would produce very serious injury to the well-being of the Society.

Mr. Kingzett made some remarks on the subject of black-balling, and also complained that a paper by Dr. Hake and himself, read before the Society in January last, had been returned to him by the Committee of Publication with suggestions that he should make certain alterations in it before it was published in the Society's Journal.

Dr. Thudichum made a similar complaint; several of his communications had been treated in the same way. He had addressed a solemn letter to the Council on the subject, but had received no reply.

Dr. Odling said that the management of the affairs of the Society was entrusted to the Council by the Fellows; some of the papers were undoubtedly delayed, but only those papers which the Publication Committee did not at first see their way to recommend for publication, and which were referred, to be specially reported on. Some sort of censorship must be exercised; it would be very unreasonable to ask them to undertake to publish indiscriminately every paper which might be presented. With regard to the black-balling, he quite agreed with Dr. Williamson that it was most important that the privilege should be exercised with the greatest discretion; but in this case it was evident that a small section of the Society, a minority of eight or nine members who regularly attended the meetings, were thwarting the wishes of the majority, since one black ball in four was sufficient to reject a candidate.

Mr. E. Riley thought it would be far better to adjourn this discussion and proceed with the business of the evening. He therefore begged to second the motion, that the Report of the President be received.

It was moved by Mr. Kingzett as an amendment, and seconded by Dr. Thudichum, that the words "unjust" and "indiscriminate" in the Report, as applied to the black-balling, be omitted.

The amendment was then put by the President, but only 12 members voted for it out of the crowded meeting; the original motion was then put and carried.

The election of Officers and Council for the ensuing year was then proceeded with, Messrs. Riley, Carteighe, and Neison being appointed scrutators. The following gentlemen were elected:—

President.—Dr. J. H. Gladstone.

Vice-Presidents.—F. A. Abel, F.R.S.; Sir B. C. Brodie, F.R.S.; Warren De La Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. Odling, M.B., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; T. Andrews, M.D., F.R.S.; W. Crookes, F.R.S.; F. Field, F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; H. E. Roscoe, Ph.D., F.R.S.; J. Stenhouse, LL.D., F.R.S.

Secretaries.—W. H. Perkin, F.R.S., and H. E. Armstrong, Ph.D., F.R.S.

Foreign Secretary.—H. Müller, Ph.D., F.R.S.

Treasurer.—W. J. Russell, Ph.D., F.R.S.

The other Members of Council are.—J. Attfield, Ph.D.; I. Lowthian Bell, M.P., F.R.S.; A. H. Church; C. E. Groves; W. N. Hartley; C. W. Heaton; T. H. Hills; David Howard; G. Matthey; J. A. Phillips; R. V. Tuson; and C. R. A. Wright, D.Sc.

A vote of thanks to the retiring President, Professor Abel, which was received with acclamation, was proposed by Professor Williamson and seconded by Dr. Warren de la Rue. There were also votes of thanks to the Officers and Council proposed by Mr. Carteighe and seconded by Mr. Tennant; to Mr. Watts and the abstractors by Dr. Odling and Mr. Crookes; and to the Auditors by Dr. Russell and Dr. Paul.

Professor Abel then dissolved the meeting, and resolved it into a special general meeting to consider some alterations in the bye-laws, when the new President, Dr. Gladstone, took the chair.

Mr. Neison proposed some verbal alterations; a discussion arose as to these resolutions being brought forward without notice; Mr. Neison ultimately agreeing to postpone the matter until the next annual meeting.

The following alterations in the bye-laws, proposed by the Council, were then put to the meeting and carried unanimously:—

In paragraph II of the bye-law relating to associates. (a). The words at the commencement of the second paragraph to be—"Associates shall pay an annual subscription of one pound." (b). The following words to be added at the termination of the second paragraph—"but they shall have the option of paying an annual subscription of thirty shillings in place of one pound, for which subscription they shall be entitled to a copy of the Society's Journal, in addition to the ordinary privileges of Fellows, with the exceptions hereinbefore specified." Also the new form of obligation to be signed by Fellows on their admission (the words in italics being the additions to the old form).

"I, the undersigned, do hereby engage that I will endeavour to promote the interests and welfare of the Chemical Society, that I will observe its Laws, and to the utmost of my power maintain its dignity, as long as I shall continue a Fellow thereof."

The meeting was then adjourned until Thursday, April 5th.

ANNIVERSARY MEETING.

[illegible]

Dr. TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND. Cr.

	£	s.	d.		£	s.	d.
To amount of subscriptions received	2,333	13	0	1877, January 23. By purchase of £23,000 Metropolitan Board of Works 3½ per cent. Stock	2,050	0	0
	£2,333	13	0	" 25. By Harrison and Sons for Printing Circu- lars, &c.	5	14	0
				" " By Macmillan and Co. for Advertising ..	2	10	5
				March 27. By Balance at Bankers	275	8	7
					£2,333	13	0
<i>Assets.</i>							
North British Railway 4 per cent. Preference Stock	1,000	0	0				
Metropolitan Board of Works 3½ per cent. Stock	2,000	0	0				
Balance at Bankers	275	8	7				
	£3,275	8	7				

A P P E N D I X.

THE Committee of the Council of the Chemical Society, appointed by a resolution passed at a meeting of Council, held on May 16th, 1867, to consider and advise upon the mode of election of Fellows into the Society, having discussed the subject at several meetings, beg leave to make the following Report :—

As bearing upon the standard of qualification for admission to the Fellowship of the Society, your Committee, from replies they have received to a circular which they addressed to all the Fellows, and from conversations they have held with different Fellows whom they chanced to encounter, have ascertained the existence among the Fellows of the Society of two very distinct views as to its nature and purposes.

Many Fellows appear to regard the Society as being by rights an association of eminent scientific men, and they accordingly look upon the Fellowship of the Society as a distinction which should be conferred only upon those who have given evidence of marked chemical proficiency, as for example, by the production of some original memoir; so that the election of any one as a Fellow of the Society should stamp him at once as being a well-trained chemist and competent investigator.

In favour of this view, it is urged that the initials F.C.S., appended to the name of any gentleman, seem to imply that his attainments have won for him a public recognition somewhat in the character of a degree, and that these initials ought to signify in reality that which they seem to imply, and which is indeed their proper signification.

It is further urged that the Fellowship of the Society is essentially an honorary distinction, although from the ease with which it can be obtained, practically by any who choose, it is a distinction but little valued by the better sort. It is, however, eagerly sought after and obtained by men who are not perhaps altogether desirable—who have certainly no claim to the title of scientific chemists—and who, in some cases, do not even join the Society from any interest they take in chemical science, but solely with the view of parading a distinction to which their merits do not really entitle them.

Moreover, from the circumstance that chemistry is pursued, not only as a science, but also as a profession and trade, the right to append the initials F.C.S. possesses a sort of trade value, exceeding its cost, to mere trading or professional chemists; as suggesting that those who

have the privilege of using these initials are better qualified men than their brethren who are not thus distinguished.

From these causes, it is said, the Fellowship of the Chemical Society has gradually sunk in public estimation; and accordingly it is very desirable that something should now be done to restore, if possible, its original prestige.

On the other hand, many Fellows are of opinion that the Society is merely an association of individuals, having joint but various interests in the progress of both pure and applied chemistry—that the object for which the Society exists is not to confer honour upon any individual whatever, but to promote the general advancement, distribution, and application of chemical knowledge; and that, as a general rule, men engaged in pursuits more or less dependent on or connected with chemistry, and taking a sufficient interest in chemistry to wish to join the Society should, unless personally objectionable, have every facility afforded them for joining it.

In favour of this view, the preamble to the charter is adduced, and especially the following paragraph: “whereas certain of our subjects “did establish and are now members of a society known by the name “of the Chemical Society, for the general advancement of chemical “science, as intimately connected with the prosperity of the manufac- “tures of the United Kingdom and for a more extended “and economical application of the industrial resources and sanitary “condition of the community,” etc.

It is further maintained that the Society, from its origin until the present time, has always been of a mixed rather than of an exclusively scientific character; that the present Fellows form quite as distinguished a body as have ever constituted the Society, and that many, at any rate, of the most distinguished individual Fellows do not feel themselves at all discredited by being associated as joint Fellows of the Society with men who are engaged or interested in chemical pursuits, but whose scientific or social position is inferior to their own.

Moreover, of scientific as distinguished from purely professional societies, the Royal Society, it is urged, is the only one of which the Fellowship is conferred in recognition of eminent scientific merit—the special science societies being practically open to all students of and workers at their respective subjects, who may wish to be elected to their respective Fellowships. To limit the Chemical Society to eminent scientific chemists would be tantamount to making it the chemical section of the Royal Society, instead of allowing it to have a distinct function and character of its own.

It is further urged that the circumstance of chemistry being to some extent a profession, so far from indicating the propriety of

making the Fellowship of the Chemical Society an honorary distinction, rather contra-indicates it. For, independently of the difficulty, or rather impossibility, of withholding or conferring the honour without doing much injustice to individuals, the Society, by professing to choose out the most worthy, would naturally be held responsible for its choice, and identified more or less with the acts of each and all of its Fellows.

Your Committee having given these different views their best consideration, are not prepared to recommend any alteration in the by-law relating to the election of Fellows, which would have the effect of confining the Fellowship of the Society to strictly scientific men.

But they think it may be advisable, although they have failed to elicit evidence of the admission of any significant proportion of unsuitable persons into the Society, to make some modification in the present by-law, with a view to increase the security against the accidental election of undesirable candidates.

They accordingly suggest that in future, or after a certain interval of time, the form of recommendation of a candidate, referred to in the first paragraph of the by-law in question, shall be required to be signed by five instead of by only three Fellows of the Society, of whom three at least instead of only one shall be required to sign from personal knowledge; and further, that in the second line of the printed form of recommendation, the words "Qualification or Occupation" shall be substituted for the words "Position, Profession, or Occupation."

At present your Committee are not disposed to advise any alteration in the second paragraph of the by-law which requires three-fourths of the votes given to be in favour of the candidate, in order to effect his election. If, however, contrary to the anticipations of the Committee, any section of the Fellows should be found to make an improper use of this requirement, your Committee would then recommend that one or other of two courses should be proposed by the Council and adopted by the Society, that is to say, that the by-law should be altered so as to render valid the election by a mere majority, or else that the by-law should be temporarily abrogated, and that, during its abrogation, the election of Fellows should be delegated by the Society at large to a Committee appointed for the purpose.

Signed on behalf of the Committee,

W. A. MILLER.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XIV.—On the Estimation of Urea by means of Hypobromite.

By A. DUPRÉ, PhD., F.R.S.

SINCE Knop in 1870 proposed a strongly alkaline solution of hypobromite of sodium for the estimation of urea in urine, the process has been worked at and modified by several chemists. Up to the present, however, neither of the methods proposed has found its way into general use, notwithstanding the rapidity and sharpness of the reaction on which they are based. This is due, I believe, to two circumstances mainly—firstly, no apparatus as yet described seems to combine ease of working with accuracy in a sufficiently high degree; and, secondly, the somewhat rapid deterioration of the hypobromite solution renders its frequent preparation a matter of necessity, and this preparation, owing to the highly pungent nature of the vapour of bromine, has been an extremely disagreeable task anywhere but in a regular laboratory. I therefore offer no excuse for making one more attempt to render the process really available for medical purposes.

*The Apparatus.**—This will be readily understood from the accompanying illustration. A burette (*a*, Fig. 1) having a lateral supply tube, put upside down into a cylinder with water, constitutes the part for measuring the gas evolved. The burette can be raised or lowered and fixed at any height by means of the clamp and rod, *b b*. The reaction between the urine and hypobromite is effected in a small flask or bottle, fitted up as for the estimation of carbonic anhydride in carbonates. The two forms which I have used, and find equally convenient, are shown in *c*, Fig. 1 and in Fig. 2. To work the apparatus, the pinch-cock, *d*, is taken off, and the burette is let down to the zero point of the division. 25 c.c. of the hypobromite solution are next put into the bottle, and the pipette (*e*) is filled with the urine in the usual manner, detaching the india-rubber tube at *f* for this purpose. Before putting the stopper back into the flask, it is advisable slightly to suck up the

* After having given directions for the manufacture of this apparatus to Mr. G. Smith, of the firm of How and Co., he informed me that they had made a very similar apparatus, some years since, for Mr. R. Apjohn of Cambridge. On referring to the *Chemical News* of January 22, 1875, I find that Mr. Apjohn's apparatus is indeed very similar to mine, and has two years' priority. It is, however, not identical, and mine will, I think, be found more complete, and much more readily worked.

urine, so that the extreme point of the pipette becomes empty, and there is no danger of a drop of urine falling into the hypobromite prematurely. This is best done by compressing the india-rubber tube attached to the pipette between the finger and thumb of one hand, above the pinchcock of course, and drawing the tube so compressed through the fingers for an inch or so. If now, before relaxing the pressure on the tube, the pinchcock is opened for a moment, the urine will be sucked up to the desired extent. If previous to use the point has been slightly greased inside, the urine will show no tendency to run back, and the pipette can be moved about without fear. The stopper with the pipette is now firmly inserted into the bottle, the india-rubber tube is slipped back over *f*, and the bottle put into a vessel with cold water. The pinchcock, *d*, is fixed on, and the burette is raised several inches, when, if all is tight, the column of water raised in the burette will remain stationary. The urine is now allowed to run into the hypobromite as rapidly as may be convenient, and a thorough mixing is effected by a gentle rotary motion of the bottle. According to Hüfner, the reaction is the more complete the more rapidly the two fluids are mixed. In from one to two minutes the reaction is almost over. The bottle should now be shaken briskly several times. This shaking causes an appreciable amount of effervescence to take place, and is the means of bringing the reaction sharply to the same point each time. In five minutes from the beginning of the experiment, the bottle is put into the cold water, the burette is let down into the cylinder for a few moments, then raised until the water inside and out is on a level, and the amount of gas collected is read off. If the arrangement Fig. 2 is preferred, the 5 c.c. urine are put into the little test tube fixed to the glass rod, the stopper

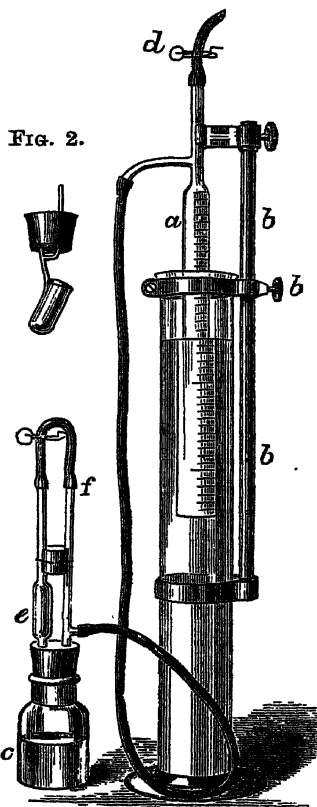


FIG. 1.

 Scale $\frac{1}{2}$.

FIG. 2.

is replaced, and the apparatus arranged and tested as before. By now inclining the bottle in one direction the little tube can be gradually emptied; by inclining it in another direction it can be filled with the hypobromite. It is thus easy alternately to empty or fill the little tube, and thus effectually to wash out all the urine. The rest is done as before.

As before stated, at ordinary temperature the reaction is virtually over in five minutes. If now the hypobromite is heated for ten minutes to a temperature of 70° C., a further evolution of gas takes place, equivalent, when 5 c.c. of a 2 per cent. urea solution have been taken, to about 0.04 per cent. of urea. Since, however, the reaction comes to an end almost equally sharply at either temperature, and in neither case do we get the whole amount of nitrogen, the heating may be entirely omitted, provided that the graduation of the burette is made accordingly. At a temperature of 65° F., and a pressure of 760 mm. I found that 5 c.c. of a 2 per cent. urea solution evolved. when the reaction was finished by heating the hypobromite to 70° C.

37.26 c.c.

37.08 „

37.08 „

Mean.. 37.14 „

or almost exactly the amount found by Messrs. Russell and West under like conditions. When the heating was omitted, 5 c.c. of the same urea solution yielded—

36.73 c.c.

36.92 „

36.73 „

36.73 „

36.73 „

36.54 „

36.73 „

36.54 „

Mean.. 36.70 „

In the before quoted paper Mr. Apjohn gives the results of nine experiments, made apparently at a temperature of 60° F., and a pressure of 760 mm., the mean of which when corrected for a temperature of 65° F. would give 36.70 c.c. gas evolved from 5 c.c. of a 2 per cent. urea solution, a figure identical with mine. If then we wish to work with 5 c.c. of urine, and at ordinary temperature, the graduations of the burette should be such that 36.70 c.c. indicate 2 per cent. of urea.

Under ordinary conditions variations of temperature and pressure may perhaps be neglected, although the error caused by such variations is not so small as the figures given by Messrs. Russell and West seem to indicate. Thus in a urine containing 3 per cent. of urea, a variation of 1 inch in the height of the barometer produces an error of 0.1 per cent. in the estimation. Now bearing in mind that at the beginning of January this year the barometer varied very nearly 2 inches in the course of a few days, it is evident that the barometer cannot always be safely neglected even for rough experiments. An error of similar amount would be produced by a rise of about 11° F., or a fall of about 13° F. In urine containing more or less of urea the errors would of course be in proportion.

Preparation of the Hypobromite.—For this I have retained the strength recommended by Knop in 1870, namely 100 grams of caustic soda dissolved in 250 c.c. water, and adding 25 c.c. bromine to the solution so produced. In order, however, to render the preparation easy, even to people unprovided with a laboratory, I have instructed Messrs. How to supply the caustic soda in bottles containing 100 grams each, and the bromine in hermetically sealed glass tubes holding 2.2 and 4.4 c.c., or enough for one and two experiments respectively. They also supply an ordinary glass stoppered bottle holding about 700 c.c. with marks at 250 and 500 c.c. capacity, and a small stoppered cylinder holding about 80 c.c., with marks at 23 and 46 c.c. capacity. If then the large bottle is filled with water up to say the 250 c.c. mark, and the contents of one bottle of caustic soda introduced, a soda-solution of proper strength is produced. When the hypobromite is wanted, say for one experiment, 23 c.c. soda-solution are put into the cylinder, and one of the smaller bromine tubes is dropped in. The cylinder is closed, and the bromine tube broken by a smart up and down shake, so as to bring the ends of the tube into sharp contact with the bottom and stopper of the cylinder. In a few moments the bromine is dissolved, and the solution has only to be cooled a little to be ready for immediate use, not a trace of bromine having escaped into the room. This plan has the further advantage that the hypobromite solution when used has always as nearly as possible the same composition, and is therefore likely to yield more uniform results. It now only remains to show by a few examples that the method as applied to urine is capable of yielding results sufficiently accurate for all practical purposes.

In every case 5 c.c. of urine or mixture were taken.

1st sample of urine, 1st experiment, 2.44 per cent. urea found.

2nd " 2.40 " "

2nd sample of urine, 1st experiment, 2.45 per cent. urea found.

2nd " 2.44 " "

The same urine diluted with various proportions of water gave—

1 part urine, 1 part water, 1.21 per cent. urea, or in original urine 2.42 per cent.

1 part urine, 3 parts water, 0.61 per cent. urea, or in original urine 2.44 per cent.

3rd sample of urine, 1st experiment, 1.77 per cent. urea.

2nd „ 1.78 „

4th „ „ 1st „ 2.78 „

2nd „ 2.80 „

The apparatus, therefore, leaves little to be desired on the score of accuracy, and is, I believe, worked with ease even by people comparatively little skilled in experimental work. A further advantage of this form of apparatus for clinical work will be found in the fact that as 25 c.c. of freshly made hypobromite are sufficient to decompose 15 to 20 c.c. of urine, two experiments may be made one after the other without changing the hypobromite. It is therefore simply necessary to wash and refill the little test tube, or refill the pipette, when the second experiment may at once be proceeded with.

It has been thought by some that it might be urged as an objection against the process that, besides the urea, there are other nitrogenised substances found in urine which evolve part of their nitrogen when treated with the hypobromite solution. It seems to me that so far from this being an objection it is rather an advantage which may be claimed for this method. The estimation of the urea in urine is of value chiefly, if not exclusively, as a measure of the amount of nitrogen eliminated. A process, therefore, which gives some portion at least of the nitrogen eliminated otherwise than in the form of urea, is for clinical purposes more valuable than a process which gives us nothing but the urea.

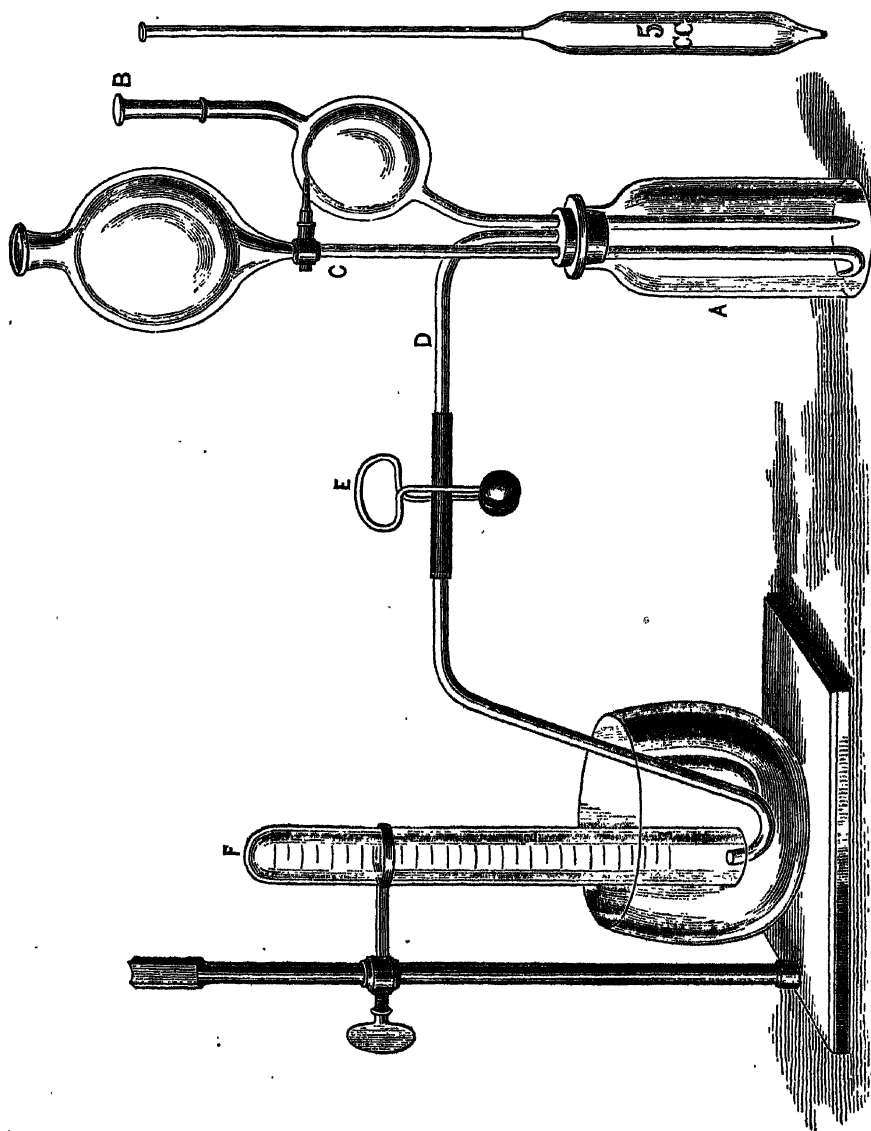
The apparatus and accessories may be obtained of Messrs. James How and Co., 5, St. Bride Street, Ludgate Circus, E.C.

XV.—On the Determination of Urea by means of Hypobromite of Soda.

By Dr. MAXWELL SIMPSON, F.R.S., and C. O'KEEFFE, F.C.S.

HAVING a great many determinations of urea to make, and not being quite satisfied with Russell and West's apparatus (*Journal of the Chemical Society*, 1874, 749), we devised one, of which a drawing is annexed, which will be found to be easily constructed, easily worked, and to give very satisfactory results.

The essentials for the construction of this apparatus are to be found in almost every laboratory. They are, an ordinary wide-mouthed bottle, A, of $1\frac{1}{2}$ oz. capacity; an india-rubber stopper with three holes; a bent pipette, B, with its extremity drawn out to a point; a narrow tube, C, about nine inches in length, surmounted by a globe, and



furnished with a glass cock, with its extremity also drawn to a point and bent upwards; a narrow gas-delivery tube, D, which can be opened and closed at pleasure by means of the pinchcock, E; a graduated tube, F (Russell and West's).

To use the apparatus, the bottle is filled with a solution of hypobromite of soda and closed with the india-rubber stopper, through the three holes of which the tubes B, C and D have already been passed. C must also contain water reaching a few lines higher than the glass cock. In closing the bottle care must be taken not to allow any air to be imprisoned between the stopper and the liquid, and that the extremities of B and C reach to the bottom of the bottle. The end of the delivery-tube, D, is now plunged a few lines below the surface of the water in the finger glass, a little hypobromite is introduced into the pipette, B, and the pinchcock, E, is opened, by which means all the air is forced out of the delivery-tube. The graduated tube, F, previously filled with water, is then brought over the extremity of the delivery-tube, and the analysis is commenced by introducing 5 c.c. of urine into the globe of C, and allowing about one-third of it to pass through the glass cock into the hypobromite solution. According as the gas rises to the top of the bottle, it forces up some of the hypobromite into the pipette. When all effervescence has ceased, the pinchcock is opened and the gas allowed to pass into the graduated tube. The pinchcock is again closed and one-third more of the urine allowed to flow into the hypobromite, and the gas forced into the graduated tube as before. When the urine has nearly reached the upper surface of the glass cock, a little water is added to it, the cock is opened, and the whole of the urine is washed into the bottle, care being taken not to allow the water to pass below the upper surface of the cock. Finally, a little hypobromite is introduced into the pipette, if necessary, the pinch-cock is once more opened, and all the gas swept into the graduated tube. The graduated tube is then transferred to a deep glass vessel containing water, the surface of the water inside and outside the tube brought to the same level, and the volume of gas read off.

In order to test the apparatus, we performed several analyses of a 2 per cent. standard solution of urea, and invariably obtained 37.0 to 37.3 c.c. of nitrogen (uncorrected). The following are the details of one of these experiments:—5 c.c. of our standard solution yielded 37.0 c.c. of moist nitrogen at 18° C., and 755 bar., equal to 33.87 c.c. of dry nitrogen at 0° C., and 760 bar. These results agree very well with those of Russell and West. The solution of hypobromite of soda used in these experiments was made according to their directions. We have ascertained that our 1½ oz. bottle contains a quantity of hypobromite sufficient for two analyses. Two determinations with

the same bottle of hypobromite yielded respectively 37.0 and 37.25 c.c. of nitrogen (uncorrected). We have also analysed several specimens of urine twice, and have always obtained the same volume of nitrogen from the same urine. We agree with Russell and West that for medical purposes it is not necessary to reduce the volume of nitrogen to 0° C. and 760 bar. in order to calculate therefrom the quantity of urea contained in a given specimen of urine. We have therefore made use of their graduated tube, which gives at once the percentage of urea, 37.1 c.c. of moist nitrogen at the temperature of the air (about 18° C.) indicating 0.1 gram of urea.

XVI.—*The Derivatives of Di-isobutyl (Preliminary Notice).*

By W. CARLETON-WILLIAMS, Assistant Lecturer on Chemistry,
The Owens College.

DI-ISOBUTYL was first obtained by Kolbe (*Ann. Chem. Pharm.*, lxi, 258) as a product of the decomposition of an aqueous solution of potassium valerate by the voltaic current.

It was afterwards prepared by Wurtz (*Ann. Ch. Phys.* [3], iv, 278) by the action of potassium or sodium on isobutyl iodide. Kolbe determined the specific gravity of the hydrocarbon to be 0.694 at 18°, and the boiling point 108°. Wurtz found the specific gravity to be 0.7057 at 0°, and the boiling point 106°. By the action of sodium on a mixture of isopropyl and amyl iodides, Schorlemmer (*Proc. Roy. Soc.*, 1876, p. 34) obtained a hydrocarbon which he has shown to be identical with di-isobutyl. Its constitution is represented by the formula, $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{matrix} \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} \begin{matrix} \diagdown \\ \text{CH}_3 \\ \text{CH}_3 \end{matrix}$.

By treating this body with chlorine, a liquid was obtained boiling between 170—180°, and having the composition $\text{C}_8\text{H}_{17}\text{Cl}$. No other derivatives have been prepared.

As our knowledge of the paraffins containing the group isopropyl twice (*e.g.*, di-isopropyl di-isobutyl, isopropylisobutyl, &c.) is slight, the study of the substitution products of di-isobutyl appeared to me to possess peculiar interest.

The di-isobutyl used in this investigation was prepared by the action of sodium on isobutyl bromide (B. P. 92°). The crude product was purified by treatment with strong sulphuric and nitric acids, then washed with water, dried over sticks of caustic potash,

and distilled with a small quantity of sodium. The pure hydrocarbon boiling at 109° was chlorinated; the product possessed a pleasant orange-like smell. It had no fixed boiling-point; on fractional distillation, the greater portion of the liquid passed over between 170 — 180° . The chlorinated product probably consists of a mixture of isoprimary and isosecondary octylic chlorides (see Schorlemmer, *Phil. Trans.*, 1872, p. 122; *Chem. Soc. J.*, xxv, 1086). A chlorine determination gave the following results:—

0.2549 grms. chloride gave $0.257 \text{ AgCl} = 25.00 \text{ p. c. Cl}$. $\text{C}_8\text{H}_{17}\text{Cl}$ contains 23.90 p.c. Cl.

This shows that the substance contained small quantities of a higher chloride.

The acetate was prepared by heating a mixture of the chloride with potassium acetate and glacial acetic acid, in sealed tubes, to 200° for six hours. The contents of the tubes were extracted with water, and the resulting light oily liquid dried over potassium carbonate. On fractional distillation one-third of the liquid came over below 130° , the larger portion distilled at 193 — 205° .

The lower boiling fraction consisting of octylene was treated with caustic potash to remove traces of isooctylacetate. It then boiled constantly at 122° , its specific gravity at 16° was 0.7526. The acetate possesses an orange-like smell; it was converted into alcohol by the action of a concentrated potash solution.

The quantity of material with which I worked was unfortunately too small to permit any attempt being made to separate the primary from the secondary alcohol by fractional distillation.

The mixture of alcohols boiled at 175 — 187° ; it was oxidised in the cold by adding small successive portions of a dilute solution of potassium bichromate and dilute sulphuric acid, until a permanent brown tinge was produced. On distilling, an acetone and an oily acid were obtained. (During this operation, my small stock of substance was seriously diminished by the bursting of a flask). The distillate was neutralised with sodium carbonate and redistilled: the acetone passed over into the receiver, and the acid remained as a sodium salt in the retort. The acid was obtained by decomposing the crude sodium salt with sulphuric acid. It is an oily liquid slightly soluble in water, and possessing a powerful and penetrating odour somewhat resembling that of valerician acid.

The silver, barium, calcium, lead and zinc salts were prepared.

Silver isocaprylate is thrown down as a white curdy precipitate, when a solution of ammonium isocaprylate is added to nitrate of silver solution. It is with difficulty soluble in boiling water, it is deposited from this solution on cooling, in the form of silky threads or small tooth shaped crystals.

- (1.) 0.2121 grms. gave 0.0917 grms. Ag.
 (2.) 0.1055 ,, 0.0461 ,,

	Found.	
Calculated for $C_8H_{15}AgO_2$.	(1)	(2)
43.03 p. c. Ag.	43.23	43.60

The barium salt was prepared by boiling barium carbonate in the acid; on evaporating the solution *in vacuo*, an amorphous skin remained; this substance could not be obtained in the crystalline form.

Calcium isocaprylate prepared by nearly neutralising the acid with milk of lime, is a most characteristic salt. By the spontaneous evaporation of the aqueous solution, it can easily be obtained in well formed crystalline plates, radiating from a central point. It is less soluble in warm water than in cold. A saturated solution of the salt at 15° becomes turbid on raising the temperature to 37°, and the density of the precipitate increases with the increase of temperature.

The salt redissolves on cooling. The following is the analysis of the crystals:—

0.1402 of the salt lost .0078 on heating to 110°, and gave 0.0379 $CaCO_3$.

Calculated for $Ca(C_8H_{15}O_2)_2.H_2O$.	Found.
Ca. 11.62	10.81
H_2O 5.23	5.56

The acetone derived from the secondary alcohol was oxidised by boiling with dilute sulphuric acid and potassium bichromate. Carbonic acid was evolved during the operation. After neutralising the distillate with sodium carbonate, and concentrating by evaporation, the silver salts were prepared by fractional precipitation.

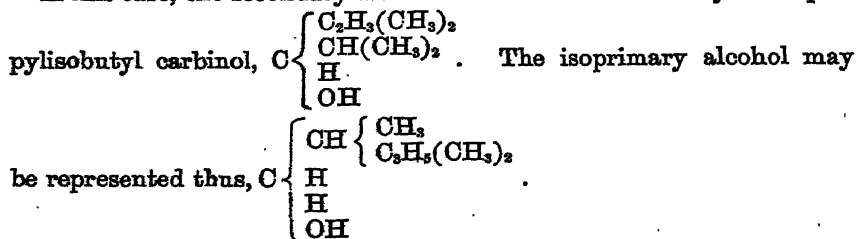
- (1.) Crystallising } 0.2054 grms. gave 0.1333 Ag.
 (2.) in minute } 0.2288 ,, 0.1469 ,,
 (3.) needles. } 0.1248 ,, 0.081 ,,

	Found.		
Calculated for $C_8H_9O_2Ag$.	(1)	(2)	(3)
64.67 p. c. Ag	64.89	64.21	64.90

It appears at first sight somewhat surprising that the only product of oxidation should be acetic and carbonic acids; but this result is easily explained, for Erlenmeyer (*N. Repert. Pharm.*, xx, 86) has shown that isobutyric acid can easily be oxidised to acetic acid and carbon dioxide. Hence it is probable that in the first instance the

ketone was converted into the isobutyric acid, and that the nascent isobutyric acid was further oxidised to acetic acid.

In this case, the secondary alcohol derived from di-isobutyl is isopropylisobutyl carbinol, C



I am at present engaged in the preparation of considerable quantities of di-isobutyl, and I hope shortly to place before the Society a more detailed account of its derivatives.

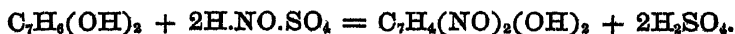
XVII.—*Dinitroso-orcin and Dinitro-orcin.*

By JOHN STENHOUSE, LL.D., F.R.S., and CHARLES E. GROVES.

ALTHOUGH numerous nitro-derivatives both of hydrocarbons and of alcohols have been prepared and examined, the nitroso-derivatives, or those which contain the NO group in place of hydrogen, were almost unknown until within a recent period, and even now the number of those which have been investigated is but small. Of the nitroso-derivatives formed directly by the action of nascent nitrous acid, one of the earliest was nitrosoethylaniline, obtained by Griess (*Deut. Chem. Ges. Ber.*, vii, 218), on mixing solutions of ethylaniline hydrochloride and potassium nitrite: subsequently, Baeyer and Caro (*Deut. Chem. Ges. Ber.*, vii, 809, 963) prepared nitrosodimethylaniline by adding concentrated hydrochloric acid to a mixture of dimethylaniline and amyl nitrite in alcoholic solution. Fitz (*Deut. Chem. Ges. Ber.*, viii, 631), instead of employing amyl nitrite followed Griess's method, and reverted to the use of potassium nitrite, substituting acetic acid, however, for hydrochloric, and in this manner obtained dinitroso-resorcin; since then, other nitroso-derivatives, such as nitroso-naphthol, nitroso-thymol, &c., have been prepared by the same method, which is analogous to the process for the formation of nitro-derivatives, by the action of a mixture of potassium nitrate and sulphuric acid on the carbon compounds.

Dinitroso-orcin.

It seemed probable that as Fitz had succeeded in preparing dinitroso-resorcin by the action of potassium nitrite and acetic acid on resorcin in aqueous solution, a corresponding derivative of orcin might be obtained by a similar method. It was found, in fact, that under these circumstances, a crystalline compound was produced, possessing properties so closely resembling those of dinitroso-resorcin, as to leave no doubt as to its nature. The quantity of dinitroso-orcin obtained in this way, however, being but small, and the product dark-coloured and far from pure, an attempt was made to prepare it by passing nitrous anhydride into a dilute aqueous solution of orcin; the liquid soon became of a deep yellow colour, and on standing some time, deposited nitroso-orcin as a pale-brown powder. The results obtained in this way were not very satisfactory from the difficulty in controlling the amount of nitrous acid passed into the solution. This difficulty was entirely obviated, however, by adding the requisite quantity of lead-chamber crystals, or nitrosyl sulphate, $\left. \begin{smallmatrix} \text{NO} \\ \text{H} \end{smallmatrix} \right\} \text{SO}_4$, dissolved in concentrated sulphuric acid, to a dilute aqueous solution of orcin, the amount of nitrosyl sulphate employed being slightly in excess of that represented by the equation,



As it is necessary to avoid, as far as possible, any admixture of nitric acid, care must be taken in the preparation of the nitrosyl sulphate. This is best effected by passing nitrous anhydride into concentrated sulphuric acid, the anhydride being obtained by acting on arsenious anhydride with nitric acid of specific gravity 1.30—1.31 at 70° C.: acid of higher specific gravity, yielding much less favourable results. The nitric acid is poured on to the arsenious anhydride in a flask, which is at once plunged into water at 70°, and the evolved gas, after passing through an intermediate flask, to retain the spray of nitric acid, &c., mechanically carried over, is passed into a weighed quantity of sulphuric acid which absorbs the nitrous anhydride. The water-bath should be maintained at 70° as long as a rapid evolution of gas continues, but as the current becomes slower, the temperature must be gradually raised to 100°. The increase of weight in the sulphuric acid represents, with sufficient accuracy, the amount of N_2O_3 absorbed, so that in this way a solution of nitrosyl sulphate of known strength is obtained. It was found most convenient to pass the gas from 200 c.c. of nitric acid into 250 grams of sulphuric acid, and then add the requisite quantity of sulphuric acid to make the solution of such strength, that every 100 parts by

weight contain 15 of N_2O_3 . In this state, although the solution deposits a large quantity of crystalline nitrosyl sulphate when cold, yet it is quite fluid when gently warmed.

After a few trials in the preparation of the nitroso-orcin in the manner described, the following proportions were found to give the best results: 20 parts of pure crystallised orcin were dissolved in 2,000 of water, and 100 of the above-mentioned solution of nitrosyl sulphate, containing 15 parts of nitrous anhydride, N_2O_3 , gradually added with constant stirring. As the liquid froths somewhat, and the nitrosyl solution is decomposed instantly on coming in contact with water, it is best to run it into the aqueous orcin solution below the surface of the liquid; this can be conveniently done by means of a long-necked funnel or a bulb-dropping tube furnished with a stopcock. In the course of a few seconds, the dinitroso-orcin began to make its appearance as a pale yellowish-brown powder, but in order to allow time for the whole of it to be deposited, the vessel containing the liquid was put aside for 18 to 24 hours. The product was then collected on a vacuum filter and thoroughly washed with cold water, in which it is almost insoluble. It must be dried at the ordinary temperature or at a gentle heat, as it is decomposed even below 100° , especially if impure. The amount of nitroso-orcin obtained in this manner was found to vary from 135 to 140 per cent. of the weight of the orcin originally taken.

As nitroso-orcin is comparatively insoluble in most solvents, and is, moreover, decomposed by heat, it was found necessary to convert it into the ammonium compound in order to purify it. This was done by suspending it in from 10 to 15 times its weight of spirit, and carefully adding alcoholic ammonia in small quantities at a time, until the brown powder was entirely converted into the green crystalline ammonium compound; finally adding a slight excess of the ammonia. In conducting this operation, some care was required to obtain a satisfactory result. When the ammonia was added to the mixture, the nitroso-orcin began to dissolve, forming a deep-brown solution, the amount of ammonia being adjusted so that not more than about one-fourth, or at most one-third of the nitroso-orcin suspended in the alcohol was dissolved; the mixture was then agitated, not only until all odour of ammonia had disappeared, but until the nitroso-orcin ammonium compound commenced to separate in green crystals. The addition of ammonia in small quantities at a time was then continued until a decided excess was present, and the odour no longer disappeared, even when the mixture was agitated and allowed to stand for 10 to 15 minutes. The pasty mass of green crystals impregnated with the brown alcoholic mother-liquor, was then thrown on a cloth and strongly pressed, the cake broken up, and decomposed by stirring

it up with water and dilute sulphuric acid, allowing it to stand some hours. The nitroso-orcin was then collected on a vacuum filter and well-washed with cold water, so as to remove adhering ammonium sulphate. It may be mentioned, that as it is not easy to obtain a perfectly homogeneous mixture of the *dried* nitroso-orcin with alcohol, it is far better to at once suspend the moist crude substance in the spirit without previously drying it, calculating the amount of spirit necessary from the amount of orcin originally operated on (1500—2000 for every 100 of orcin originally taken). In one instance, where, instead of adding the alcoholic ammonia gradually in the manner just described, a considerable excess was at once poured in, the whole of the nitroso-orcin dissolved, forming a deep-brown solution, but the green ammonium salt did not crystallise out even on long standing. We have not, as yet, investigated the nature of the reaction which takes place under these circumstances. Another treatment or two with alcoholic ammonia serves to remove all soluble impurities from the nitroso-orcin, yielding a product which is of a very pale colour, but as it is liable to contain some lead sulphate derived from the concentrated sulphuric acid employed in the preparation of the nitrosyl sulphate, it is advisable to dissolve it in a dilute solution of sodium hydrate, and precipitate the filtered liquid by an acid. This was most conveniently done by suspending the purified dinitroso-orcin in 10 to 15 parts of water, and adding a solution of sodium hydrate until nearly the whole was dissolved. The solution was then filtered and strongly acidulated with dilute sulphuric acid. The precipitate thus produced was of a somewhat darker colour than that obtained by decomposing the ammonium salt, which is probably due to the larger size of the crystals.

The dinitroso-orcin, dried *in vacuo* at the ordinary temperature, was submitted to analysis with the following results, the nitrogen being determined by Zulkoffsky's modification of Dumas' method:—

- I. .254 gram substance gave .394 gram of carbonic anhydride and .107 gram of water.
- II. .275 gram substance gave .425 gram of carbonic anhydride and .108 gram of water.
- III. .376 gram of substance gave 44 c.c. of nitrogen at a temperature of 7.25°, and a pressure of 756.7 mms. (cor. to 0° C.), equivalent to 42.3 c.c., or .05307 gram of nitrogen.

		Theory.	I.	II.	III.	Mean.
C ₇	84	42.00	42.30	42.15	—	42.22
H ₈	8	4.00	4.68	4.36	—	4.52
N ₂	28	14.00	—	—	14.11	14.11
O ₂	80	40.00	—	—	—	—
	200	100.00				

These numbers agree sufficiently with those required by the formula $C_7H_5N_2O_5$ or $C_6H(CH_3)(NO)_2(OH)_2 + OH_2$, to show that the substance is dinitroso-orcin.

Pure dinitroso-orcin, prepared by the decomposition of the sodium or ammonium compound, is a pale-coloured crystalline powder, but it may be obtained in distinct crystals by adding a solution of 4 parts of orcin in 400 of water to a dilute aqueous solution of nitrous acid (made by pouring 20 parts of the nitrosyl sulphate solution containing 3 of N_2O_5 into 1600 of water). The liquid becomes deep-yellow, and on standing for 24 hours, deposits the dinitroso-orcin in sharply-defined transparent prisms of a deep-yellow colour. It is almost insoluble in water, alcohol, ether, benzene, &c., but dissolves in hot glacial acetic acid, and is reprecipitated, apparently but little altered, on diluting the solution with water. It dissolves when boiled with alcohol, but undergoes decomposition at the same time. Cold concentrated sulphuric acid dissolves it with deep-red colour, and the solution, if at once poured into water, deposits unaltered nitroso-orcin; on heating the solution in the concentrated acid, however, or even on allowing it to stand for some time, it becomes decomposed. When nitroso-orcin is heated in a narrow tube, it begins to turn dark rapidly at 110° , but without fusing, and at 140° becomes almost black. Heated rapidly on platinum-foil, it fuses and decomposes, but without deflagration.

The potassium-, sodium-, and ammonium-derivatives of dinitroso-orcin are green crystalline compounds, soluble in water, but only slightly soluble in alcohol. The ammonium compound is decomposed by prolonged contact with alcoholic ammonia. The derivatives containing the metals of the alkaline earths and the heavy metals are brown amorphous insoluble precipitates.

Dinitro-orcin.

Strong nitric acid acts readily on nitroso-orcin, especially when heated, forming trinitro-orcin, together with some oxalic acid. With dilute nitric acid in the cold, however, the action was different, dinitro-orcin and oxalic acid being produced, but only traces of trinitro-orcin. When finely-powdered nitroso-orcin was added to 4 times its weight of nitric acid of specific gravity 1.3, taking care to keep the mixture cool by immersing the beaker in cold water, it gradually acquired a reddish-brown colour. The odour of nitrous fumes soon became apparent, and in the course of 5 or 10 minutes it solidified to a pasty crystalline mass, which had to be stirred up at frequent intervals, so as to prevent its becoming warm, otherwise much trinitro-orcin would have been formed. In this operation, it is not

necessary to employ pure dry nitroso-orcin; the crude moist substance answering every purpose, adjusting the amount of acid so that for every 100 parts of orcin originally taken, about 550 of the nitric acid be employed. After standing 20—24 hours, the product, which had become of an orange colour, was mixed with an equal bulk of cold water, collected on a vacuum-filter, and well washed with cold water. The dry product was then dissolved by agitation with cold ether, in which it is readily soluble, filtered, and evaporated to dryness in the water-bath. The dinitro-orcin was finally purified by two or three crystallisations from boiling spirit (5 parts), dried at 100°, and analysed.

I. .465 gram substance gave .677 gram carbonic anhydride and .130 gram water.

		Theory.	
C ₇	84	39.25	39.70
H ₆	6	2.81	3.10
N ₂	28	13.08	
O ₈	96	44.86	

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From these numbers it is evident that the new compound is dinitro-orcin, C₇H₆N₂O₈ or C₆H(CH₃)(NO₂)₂(OH)₂, derived from dinitroso-orcin by the displacement of the NO group by NO₂.

Dinitro-orcin crystallises in deep yellow rhomboidal plates, which are almost insoluble in cold water, more soluble in boiling water, but crystallising out again almost entirely on cooling. It is very soluble in ether, and requires about 18 parts of alcohol at 15° C. for solution. It is also slightly soluble in carbon bisulphide, and readily in hot benzene, but almost insoluble in light petroleum. Dinitro-orcin melts at 164.5°, 2° higher than trinitro-orcin, but, unlike the latter, which explodes a little above its fusing point, dinitro-orcin may be heated to above 190° without alteration, and with care may even be sublimed at a somewhat higher temperature. Heated rapidly on platinum foil it fuses and deflagrates. It is slightly soluble in concentrated sulphuric acid, with a yellow colour, but when heated with the acid, it dissolves with effervescence, forming a deep orange-coloured solution, which does not yield a precipitate on the addition of water. It dissolves in hot concentrated nitric acid, and is at the same time converted into trinitro-orcin.

The derivatives which dinitro-orcin forms with the alkali-metals, as also the corresponding ammonium-compound, are very soluble in water, and difficult to obtain in the crystalline state; they are of an orange-red colour. When dinitro-orcin is boiled with water and silver oxide or carbonate, it is decomposed, the silver being reduced,

and forming a metallic mirror on the side of the vessel. With barium, it forms two compounds, one of which is almost insoluble in water, and of a deep crimson colour; the other, which forms long silky needles of a bright yellow colour, is sparingly soluble in boiling water, but crystallises out almost entirely on cooling. The crimson barium compound may be obtained by adding an excess of an aqueous solution of barium hydrate to a solution of dinitro-orcin in spirit; on boiling the mixture, the salt is thrown down as a crystalline powder. It dissolves on boiling it with water and excess of dinitro-orcin, and the solution, on cooling, deposits the acid salt in orange-yellow needles. In order to obtain them free from dinitro-orcin, however, it is best to operate in the following manner:—2 parts of dinitro-orcin are dissolved in 40 of alcohol, and the solution divided into two parts, one of which is slightly less than the other. The smaller portion is then heated, diluted with its own bulk of hot water, and boiled; a cold saturated aqueous solution of barium hydrate is now added in slight excess (a quantity rather more than equal in volume to the solution of dinitro-orcin in alcohol and water), the mixture is allowed to cool in a closed vessel to prevent formation of barium carbonate from absorption of carbonic anhydride from the atmosphere, and the precipitate collected on the vacuum-filter and thoroughly washed with cold water. The crimson basic salt thus obtained is converted into the acid salt by boiling it with a considerable quantity of distilled water, and adding the second larger portion of the alcoholic solution of dinitro-orcin; the crimson salt soon dissolves, and the clear liquid, on cooling, solidifies to a mass of the needle-shaped crystals of the acid barium salt. A second crystallisation from boiling water suffices to purify it. Determinations of the amount of barium in the salt were made.

I. .442 gram substance gave .178 gram barium sulphate.

II. .441 " " " .177 " " "

These results correspond to 23.69 and 23.61 per cent. of barium, whilst the formula, $\left. \begin{matrix} \text{C}_7\text{H}_4(\text{NO}_2)_2\text{OH} \\ \text{C}_7\text{H}_4(\text{NO}_2)_2\text{OH} \end{matrix} \right\} \text{BaO}_2 + \text{OH}_2$, requires 23.60 per cent.

We have found that the nitrosyl-sulphate solution described in the earlier part of this paper, may be employed advantageously in the preparation of other nitroso-derivatives, giving much better results than those obtained with potassium nitrite and an acid. Resorcin, for instance, treated in this manner, gives 96 per cent. of the theoretical amount of dinitroso-resorcin, whilst Fitz only obtained 80 per cent. by treatment with potassium nitrite and acetic acid. Again, Baeyer and Caro (*Deut. Chem. Ges. Ber.*, vii, 967), by treat-

ing an aqueous solution of phenol with potassium nitrite and acetic acid at a temperature of 0° , and allowing the mixture to stand, obtained a black tarry deposit and a brown solution from which some nitroso-phenol was extracted by treatment with ether, &c. We have found, however, that on adding the nitrosyl-sulphate solution in rather more than the theoretical quantity to a solution of phenol in 30 times its weight of water, the liquid acquires a brown colour, and in a few minutes deposits a large quantity of almost pure nitroso-phenol in pale brown crystals, which, after the mixture has been allowed to stand 20 minutes, should be collected, well-washed, and dried. If the mixture be allowed to stand for any length of time before collecting the crystals, they become contaminated with a black tarry substance which is slowly deposited. Equally favourable results were obtained in the preparation of nitroso-thymol, and nitroso-naphthol.

XVIII.—*Note on Gardenin.*

By JOHN STENHOUSE, LL.D., F.R.S., and CHARLES E. GROVES.

GARDENIN was discovered by one of us (*Stenhouse, Phil. Trans.*, 1856, cxlvi, 155, and *Ann Chem. Pharm.*, xcvi, 316) some 20 years ago in "dekamali gum," a resinous exudation from the *Gardenia lucida*, but the amount of gardenin obtained at that time was insufficient to make a satisfactory analysis, the quantity of resin operated on being but limited. About three years ago, however, we had a larger sample of the resin, enabling us to obtain a few grams of the gardenin in the pure state. The resin from the *Gardenia lucida* has been fully described both by Dymock (*Pharm. Journ.* [3], vii, 491), and by Flückiger (*ibid.*, p. 589), the latter of whom, moreover, extracted the gardenin and analysed it.

We found that the best method of obtaining the crude gardenin was to boil the resin with alcohol, filter the solution to separate the insoluble residue, consisting chiefly of small fragments of bark and wood, and allow it to cool. It then deposited almost the whole of the gardenin in slender, pale-yellow needles, which were collected and washed with cold spirit, to free them from the amorphous greenish-yellow resin, which forms by far the larger portion of dekamali gum. These needles, however, even after several crystallisations from alcohol, were found to be still impure, being contaminated with a colourless substance of low melting point, somewhat resembling a fat in appear-

ance. After repeated trials in various ways, it was found that this impurity might be removed by means of light petroleum. A boiling saturated solution of the gardenin in alcohol was allowed to cool, and the almost pasty mass of crystals was agitated with light petroleum at a temperature of about 30°, the clear liquid poured off, and the residue again agitated with petroleum, repeating the operation several times. The gardenin was finally purified by alternate crystallisation from hot benzene, in which it is readily soluble, and from alcohol.

When pure, gardenin forms brilliant deep yellow crystals, which melt at 163—164°. Dried at 100°, and burnt in a current of oxygen it gave the following results.

I. .249 gram of substance gave .567 gram carbonic anhydride, and .119 gram of water.

II. .202 gram of substance gave .457 gram carbonic anhydride, and .102 gram of water.

		Theory.	I.	II.	Mean.	Flückiger.
C ₅	60	61.86	62.12	61.70	61.91	59.47
H ₅	5	5.16	5.31	5.60	5.45	6.71
O ₂	32	32.98	—	—	—	—

97 100.00

Flückiger's numbers do not agree with these, but as the specimen he analysed had merely been purified by repeated crystallisation from spirit, it is not impossible that it was contaminated with traces of the colourless fatty substance mentioned above. This is rendered very probable by the much lower melting point (155°) which he obtained.

It was stated in the earlier paper (Stenhouse, *loc. cit.*) that when gardenin is digested with concentrated nitric acid, it is rapidly decomposed, picric acid, but no oxalic acid being produced. On repeating the experiment, however, we found this to be incorrect: gardenin, when boiled with nitric acid, dissolves with evolution of nitrous fumes, forming a yellow solution, which, on evaporation, leaves a yellowish residue; this, however, on careful examination, proved to be quite free from trinitrophenol. It was noticed, in making this experiment, that at the moment the gardenin came in contact with the nitric acid, it assumed a brilliant crimson colour before dissolving. The attempts made to isolate the red substance thus formed were ultimately successful: 1 part of gardenin was dissolved in about thirty times its weight of boiling glacial acetic acid, and after being rapidly cooled two parts of nitric acid of sp. gr. 1.45 were added to the clear solution. In a few seconds hair-like crimson needles began to form, very different in appearance from gardenin. At the expiration of 5 minutes, the mixture, which was kept cold, had solidified to a pulp of needles.

It was then mixed with about 150 parts of cold water, and the gelatinous precipitate collected after it had stood a few minutes. The pasty red mass, after being well washed, was pressed into a cake and removed from the filter before drying, for it was found that if allowed to dry on the filter it adhered so firmly to the paper that it was very difficult to remove it. Gardenin yields nearly 90 per cent. of its weight of this substance, which is insoluble in water and dilute acids, but readily soluble in alkaline solutions, and reprecipitated, on the addition of an acid. We have provisionally named it *gardenic acid*. It is free from nitrogen, and after being purified by boiling with spirit, in which it is but very slightly soluble, and crystallisation from glacial acetic acid, it was found to melt at about 236°. If the nitric acid is allowed to act on the glacial acetic acid solution of gardenin for a considerable time, or on the gardenic acid itself, it becomes changed to an orange-coloured substance much more soluble in alcohol than gardenic acid.

At present the amount of gardenin at our disposal is too small to permit a thorough examination of these new compounds, and other derivatives of gardenin. As they appear, however, to be of some interest, we have made arrangements to obtain a considerable quantity of dekamali gum from India, and hope ere long to be able to continue the investigation.

Note on Ginger.

As the nature of the resinous substance contained in ginger, and to which its pungent character is due, has not as yet been investigated, it seemed possible that a careful examination of it might lead to interesting results. The few preliminary experiments we made, however, did not appear very promising.

The ground ginger, *Zingiber officinale*, from Cochin China, was extracted by boiling with alcohol, and the solution evaporated after filtration. The viscid residue had a strong odour of ginger, and when heated in a current of steam yielded a small quantity of essential oil lighter than water. A portion of the extract was fused with three times its weight of soda, and the product neutralised with sulphuric acid, and extracted with ether in the usual way. The ethereal solution, on evaporation, left a mass of crystals impregnated with a dark coloured liquid; these, after purification by pressure and two or three recrystallisations from water, were examined and proved to be protocatechuic acid. They gave the ordinary well-known reactions of protocatechuic acid, and fused at the same temperature. On heating them with excess of bromine in a sealed tube, carbonic anhydride and tetrabromopyrocatechin were formed.

XIX.—*Isomeric Nitroso-terpenes.*

By WILLIAM A. TILDEN, D.Sc. (Lond.), and
W. A. SHENSTONE, F.C.S.

AN immense number of hydrocarbons, described as terpenes, and having the composition and molecular weight indicated by the formula $C_{10}H_{16}$, are known, but our knowledge of their properties and constitution is at present extremely imperfect, and some method by which they may be identified and classified is very desirable.

The nitroso-terpene obtained by Tilden (*Chem. Soc. J.*, 1875, p. 514), from common dextrogyrate turpentine oil, stands alone at the present time as an example of a well-defined crystalline derivative obtained from a terpene by a direct process of substitution. By preparing and studying in detail a number of the corresponding isomeric compounds from other hydrocarbons of the same class, we hope to be able to throw some light on their mutual relations.

The present paper contains an account of the methods employed. The crystallographic characters of the nitroso-terpenes hitherto obtained are under investigation by Professor N. Story-Maskelyne, and a complete description of these products is reserved until their examination shall be finished.

We have operated upon terpenes obtained from various essential oils, which were supplied from trustworthy sources, and were believed to be perfectly genuine and unadulterated. The oils of juniper, savin, caraway, and sage were of English production, those of lemon, bergamot, and sweet orange (*Essence de Portugal*) were the best obtainable in commerce. These oils contain terpenes which are divisible into two classes. In the one we have those, of which common turpentine is the type, boiling under ordinary pressure at 160° or thereabouts. In the other class we have terpenes represented by the hydrocarbon from orange-peel, boiling at 174° . The turpentines are said to yield acetic and terephthalic acid when oxidised, whilst it has been shown by Wright that hesperidene (orange-peel terpene) yields neither toluic nor terephthalic acid, but a body resembling camphor.

Preparation of the Nitroso-chlorides of the Terpenes.

The preparation of these compounds is the first step towards the production of the nitroso-substitution derivatives. The general formula of the nitroso-chlorides is $C_{10}H_{16}(NO)Cl$, and they are formed by the direct union of nitrosyl chloride with the hydrocarbon. They cannot, however, be regarded as mere products of addition containing nitrosyl

chloride united to the terpene in the same manner as water of crystallisation is united with a salt. For none of them are in the slightest degree affected by contact with water or alcohol, both of which instantly decompose not only nitrosyl chloride itself, but various molecular compounds which nitrosyl chloride forms with other bodies, such as anthracene.

The nitrosyl chloride required for the preparation of these compounds is obtained, as formerly described, by acting upon common salt with "chamber crystals," or with sulphuric acid saturated with nitrous anhydride. We find it best to place in a flask, having a side tube to convey away the gas, a quantity of common salt wetted with strong hydrochloric acid, and to allow the nitrous sulphuric acid to drop in upon the mixture, which after a time may be gently heated.

One important condition for the successful preparation of the nitroso-chlorides of the terpenes is that the temperature of the liquid be kept throughout the experiment at a few degrees below zero. In operating upon rectified turpentine oil as in the original experiments, some difficulty was experienced in preventing the hydrocarbon from becoming heated under the influence of the nitrosyl chloride. We now find that the process becomes more manageable if the hydrocarbon is diluted with several times its volume of some solvent, such as chloroform or spirit of wine, the choice of the liquid being determined by a preliminary experiment on a small scale.

The process we now adopt is one or other of the following. The terpene is dissolved in three or four times its bulk of chloroform,* cooled by means of ice and salt to about -10° , and then saturated with nitrosyl chloride passed in at such a rate that the temperature is not caused to rise appreciably. The liquid, which becomes bright green, is tested from time to time by mixing a few drops of it with several times its bulk of spirit of wine. When a white crystalline precipitate makes its appearance, the quantity of which is not increased perceptibly when a subsequent testing is made after the further action of the gas, the whole of the chloroform solution is poured into two or three times its volume of methylated spirit, and allowed to stand for half an hour. The ensuing precipitate, which is quite white, and which consists of minute prismatic crystals, is then filtered off, washed with rectified spirit, and dried by pressure and exposure to the air.

This process we have found applicable to some varieties of turpentine, and especially to the terpene from juniper oil, but not to the terpenes from caraway, bergamot, lemon, and sweet orange. In these latter cases the hydrocarbon is mixed with five or six times its bulk of methylated spirit, a quantity generally sufficient to dissolve nearly the whole of it, and the liquid is then cooled to about -10° . On

* In the case of common turpentine, half its bulk of chloroform is sufficient.

passing nitrosyl chloride gas into this solution, it assumes a pale green colour, and after a time becomes almost pasty, from the formation of crystals of the nitrosochloride, slight effervescence attending the end of the operation. This precipitate is collected and pressed from a small quantity of green oily matter, and then washed with spirit. If required in a state of perfect purity, it may be dissolved in chloroform and crystallised out again by mixing the solution with alcohol.

The Nitroso-terpenes.

1. *Nitroso-australene*.—Ordinary American dextrogyrate turpentine oil was employed. Those portions which come over below 160° or 161° may be used. Different samples vary slightly in their action upon the polarised ray. The first specimen operated upon had the specific rotatory power* $[\alpha]_D = +17.5^{\circ}$. The nitroso-chloride, the analysis of which has already been published (*loc. cit.*) melts at about 103° , but is thereby decomposed, yielding a brown liquid, which does not solidify on cooling. When this substance is warmed with rectified spirit, small quantities of alcoholic potash being added till the whole of it has just dissolved, it loses the elements of hydrochloric acid, and is converted into nitroso-australene (designated in the former paper simply nitroso-terpene). The alkaline liquid being neutralised and evaporated, yields crystals of this compound, the analysis and crystallographic characters of which have already been published. It melts at 129° (corr.) and its alcoholic solution has no action on polarised light.

2. *Nitroso-terebenthene*.—French turpentine was re-distilled, those portions being collected which passed over between 156° and 160° . A column 100 mm. long of this liquid was found to deviate the polarised ray 33.7° to the left. When treated with the nitrosyl chloride, this hydrocarbon yields a much smaller quantity of nitroso-chloride than the dextrogyrate turpentine. And the reason of this seemed to be that a greater amount of heat is developed, so that it is more difficult to prevent the liquid from becoming suddenly hot, and so destroying the product. It is interesting to notice, in connection with this fact, that the specific rotatory power of this hydrocarbon in a state of partial purity, as observed by us, is more than twice as great as that of the dextrogyrate variety, though in the opposite direction. The numbers given by Berthelot are for pure australene $[\alpha]_D = +21.5^{\circ}$, and for pure terebenthene $[\alpha]_D = -42.3^{\circ}$.

The nitrosochloride obtained has properties similar to those of the

* The rotatory powers of the substances mentioned in this paper were determined by means of a Wild's polaristropometer, using as source of light a Bunsen-flame tinged yellow by means of a bead of sodium chloride and borax.

corresponding compound obtained from dextrogyrate turpentine. It is a white crystalline powder, which, when acted upon by alcoholic potash yields nitrosoterebenthene of the formula, $C_{10}H_{18}(NO)$. It agrees in most of its characters with nitroso-australene. Thus its alcoholic solution is optically inactive, and the melting point is the same, the actual determination being 128.8° (corrected). The crystals obtained by slow evaporation of its alcoholic solution are, however, easily distinguishable from those of nitroso-australene obtained in the same way. Their different appearance is, however, probably not due to any fundamental difference of crystalline structure, but to a peculiarity of habit, the cause of which has not yet been found out. Their description must be postponed until the measurements are complete, but we may mention that, although the specimens in our possession have been several times recrystallised, we have not observed the formation of crystals having the same appearance as those of the first discovered compound, nitroso-australene.

3. Terpenes from oil of sage (*Salvia officinalis*). We are indebted to Mr. M. M. Pattison Muir for small quantities of two terpenes from this essential oil.

A. Boiling point, $158-160^{\circ}$. 100 mm. gave a rotation of 32.2° to the left. This substance behaves in every respect like the terpene from French turpentine. The crystals of the nitroso-derivative have the same aspect and melting point (129°), and the alcoholic solution is optically inactive. The observed rotatory power of this terpene being so nearly equal to that of terebenthene, we believe these two hydrocarbons to be not merely isomeric but identical.

B. Boiling point, $168-176^{\circ}$. 100 mm. rotate the plane of polarisation 17.7° to the left. We have not been successful in obtaining a solid nitroso-derivative from this hydrocarbon. The action of the nitrosyl chloride causes effervescence, and the production of brown oily substances. It is not improbably a mixture containing polymeric hydrocarbons.

4. Terpene from oil of juniper (*Juniperus communis*). English oil of juniper was submitted to fractional distillation, and about one-third of the whole was separated, boiling below 160° . This portion consists of the terpene sufficiently pure. It showed a rotation of about 1° to the left for a column 100 mm. long. When diluted with chloroform and treated with the gas, this hydrocarbon gave a crystalline nitroso-chloride much more readily and in larger quantity than either of the terpenes previously described. After washing and reprecipitation from chloroform it was analysed. .3701 gram gave .2613 gram of $AgCl$, corresponding with 17.46 per cent. of chlorine. $C_{10}H_{18}NOCl$ requires 17.6 per cent. Decomposed with alcoholic potash in the usual way, it gave a crystalline nitroso-compound, which we believe

to be identical with nitroso-terebenthene. It was found to melt at 128.5° . Its alcoholic solution is optically inactive, and the crystals have the same form as those of nitroso-terebenthene. The hydrocarbons, however, from which these two compounds are obtained, by no means agree in physical properties, the turpentine having a much greater rotatory power than the juniper terpene, and giving out a greater amount of heat under the influence of the nitrosyl chloride.

Comparing together the four terpenes thus far described, we find that, as regards the facility with which they yield nitrosochlorides, they stand in the inverse order of their action on polarised light, the juniperene, which is almost destitute of such action, giving out less heat, and furnishing a larger yield of nitroso-chloride than the others. Next to juniperene comes right-handed turpentine, and lastly the left-handed turpentine and sage terpene, which are equal.

With these facts in view we thought it probable that, by destroying the rotatory power of an active hydrocarbon, we should get a liquid which would yield a nitroso-derivative very readily. We have, therefore, treated a quantity of both dextro- and lævo-gyrate turpentine with sulphuric acid, and after washing submitted the product to fractional distillation. The fractions which came over at $156-159^{\circ}$, and of which, by the way, only a very small quantity was obtained, were quite colourless and destitute of rotatory power, and correspond with the hydrocarbon which has been described as terebene. This liquid, submitted to the action of nitrosyl chloride under various conditions, gave no crystalline nitroso-chloride. The attempt will be renewed, but for the present it is sufficient to state that terebene certainly differs from the terpenes in its behaviour with this reagent.

5. *Nitroso-hesperidene*.—*Essence de Portugal* submitted to distillation yielded about three-fifths of its bulk, boiling at $174-175^{\circ}$. A column 100 mm. long gave a rotation of 85.9° to the right. Nitrosyl chloride passed into a mixture of the hydrocarbon, with about five volumes of methylated spirit, caused a copious crystalline deposit of nitroso-chloride. After thorough washing with spirit of wine, the chlorine was determined. .8748 gram gave .6221 gram of silver chloride, indicating 17.5 per cent. of chlorine. This agrees with the formula, $C_{10}H_{16}NOCl$, which requires 17.6 per cent.

When treated with alcoholic potash this compound behaves differently from the nitrosochlorides hitherto described. It gives by this process no crystalline nitroso-compound, but a brown, viscid, oily body, which we have not felt disposed to examine more closely at present, but which almost certainly consists of or contains a liquid nitroso-hesperidene isomeric with the crystalline variety. This latter we have succeeded in obtaining, though at great expense of material, by another process. The dry nitroso-chloride melts at about 103°

and forms a green liquid, which, if kept at the melting point even for a few seconds, enters into violent ebullition from the escape of gas, and yields nothing but brown viscid products. If, however, the melted chloride is cooled quickly by immersing the tube in cold water, a semi-solid crystalline mass results. The solid portion does not, however, consist of unaltered nitroso-chloride, but of the nitroso-terpene deprived of the elements of hydrochloric acid, a little of which escapes in fumes. The liquid products formed at the same time have not yet been examined. They are brown and have a peculiar aromatic odour.

In order therefore to prepare crystallised nitroso-hesperidene, the nitroso-chloride is heated in test-tubes in portions not exceeding about a gram each. As soon as the compound is completely melted and the liquid becomes yellowish, the tube is at once plunged into cold water. After standing a few hours, the honey-like mass in each tube is dissolved out with alcohol and the united solutions set aside. Large flat, probably orthorhombic, prisms are deposited. They are more than twice as soluble in alcohol as any of the compounds previously described, and the tendency of the compound to form large crystals is quite remarkable. It may be sublimed, but an attempt to determine the vapour-density in the barometer vacuum of Hofmann's apparatus failed, as the temperature of boiling aniline vapour was not sufficiently high to volatilise it, and it is first polymerised and then becomes brown at higher temperatures.

In one characteristic, this compound differs notably from those previously described. Although the terpene from which this compound is derived is dextrorotatory, the alcoholic solution of this derivative is lævorotatory. 1 part of nitrosohesperidene dissolved in 9 parts by weight of alcohol of 84 per cent. gave a solution the specific gravity of which at 10° was '8609. 200 mm. of this solution gave as the mean of four observations $\alpha_D = -6^\circ 19'$, whence $[\alpha]_D = -36.6^\circ$.

Nitroso-hesperidene dissolved in rectified spirit gives no precipitate with hydrochloric acid gas or solution. Its chloroform solution mixed with bromine leaves, after evaporation, a semi-crystalline mass of dibromide, $C_{10}H_{15}(NO)Br_2$.

The melting point of hesperidene was in one case found to be 70.1° , and another sample, probably purer, 71° (corr.).

The results of its combustion are as follows:—3536 gram gave .9340 gram of CO_2 , and .2964 gram of OH_2 .

	Calculated.	Experiment.
C_{10}	72.72	72.02
H_{15}	9.09	9.3
NO.....	18.19	—

6. *Terpene from Caraway*.—2½ lbs. of English oil of caraway (*Carum carui*) submitted to distillation gave about 7 fluid ounces of hydrocarbon boiling below 178°, and 100 mm. column of which gave a rotation of + 11°.

This terpene was treated in precisely the same manner as the hydrocarbon from orange-peel. It gave a nitrosochloride, the chlorine of which was determined and found to agree with the requirements of the general formula $C_{10}H_{16}NOCl$. After heating in the manner already described, it yields a crystallisable nitrosoterpene which is in every respect identical with that obtained from hesperidene. It melts at 71°, rotates the polarised ray in the same direction and to the same extent, and in solubility and crystalline form agrees fully with that compound.

7. *Bergamot*.—The best commercial oil of bergamot (*Citrus bergamia*) was submitted to distillation. About three-fifths came over below 190°. This gave about a fourth of its bulk below 180°, and this, after treatment with sodium for some hours, came over almost entirely below 176°. 100 mm. of this hydrocarbon rotates 75·6° to the right. When treated with nitrosyl chloride in the same manner as hesperidene, it gave a nitroso-chloride which melted at about 98°, and after heating gave a honey-like mass from which the nitroso-compound was extracted. This compound, like nitroso-hesperidene, melts at 71° and is levogyrate, but when crystallised from spirit it gives none of the broad flat prisms so characteristic of the compounds from orange and caraway. At present it has been obtained only in concentric or parallel groups of very long thin prisms, which have not yet been examined with the goniometer.*

8. *Lemon*.—Essence of lemon gives a large quantity of a terpene boiling at 173—176°, and of which 100 mm. were found to rotate the polarised ray 61·5° to the right. This terpene does not yield the nitrosochloride readily by any process at present tried. A few grams, however, have been obtained and the chlorine determined. It gave 17·13 per cent., thus agreeing with the general formula. It does not yield a crystalline product after treatment with alcoholic potash, and the result of heating the small quantity in our possession was unsatisfactory. Further information about this compound has therefore yet to be obtained.

9. *The Essential Oil of Savin* (*Juniperus Sabina*), a coniferous plant, was thought likely to yield derivatives similar to those of turpentine and juniper, but at present attempts to produce them have been unsuccessful.

* Since the above was written, we have prepared a large quantity of this compound, and we now find that it yields crystals of the same form as the nitroso-compounds from the terpenes of sweet orange and caraway.

We believe the results we have described are sufficient to show that the method we have adopted is competent to fulfil the purpose to which we have endeavoured to apply it, namely, to distinguish the isomeric terpenes from one another and to effect a classification of these bodies. We believe that the result of the further application of this method will be to show that a great many of the natural terpenes are merely physical isomerides not differing from one another in chemical constitution, and we think it probable that the number of distinct chemical species, at least among the natural terpenes, will prove to be not so great as is sometimes supposed.

Nitroso-australene from common turpentine, and nitroso-hesperidene from sweet orange peel, may be regarded as typical compounds. Experiments, which have for their object the determination of the rational formulæ of these compounds, are now in progress.

XX.—*Preparation of Copper-zinc Couples.*

By J. H. GLADSTONE, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and ALFRED TRIBE, F.C.S., Lecturer on Chemistry in Dulwich College.

IN 1872 we communicated to the Royal Society the fact that zinc on which copper or some other negative metal was deposited in a spongy condition decomposes water at the ordinary temperature. This association of metals we subsequently termed the *copper-zinc couple*, an agent which has since been instrumental in the discovery of many new compounds and reactions.

Observations on the preparation of the couple have been published by Professor Thorpe and by ourselves, but the contemplation of a still larger extension of its use induced us to study more in detail the effect of the quantity and condition of the negative metal, with the practical object of arriving at the best formula for its preparation.

From the beginning we have used zinc in the form of foil. This condition possesses advantages. It gives a greater surface for equal weights than granulated zinc does, and admits of the use of a definite amount of surface, which is absolutely necessary where comparative results are required. The foil has generally been obtained from Messrs. Hopkin and Williams, 16, Cross Street, E.C. It contains about 1 per cent. of lead, the average amount of that metal which we found in several specimens of commercial zinc, and its thickness should be such that a square decimeter weighs about 2 grams.

Preparation of the Couple.

Well crumple the required quantity of foil, and cut it into pieces of from 100 to 600 square millimeters. Place these in a vessel suitable for the projected operation, add a solution of copper sulphate, and allow the whole to remain until decolorised. Pour away the liquid, which has become a solution of zinc sulphate, and thoroughly wash the couple so made with water. Should more copper be required than is obtainable from the volume of copper sulphate solution necessary for the complete immersion of the zinc, another "deposition" can be effected by replacing the solution of zinc sulphate produced in the first operation by more copper sulphate.

Influence of Quantity and Condition of the Copper.

When zinc displaces copper from equal volumes of its sulphate of different strengths, the quantity of the metal deposited varies of course with the strength of the copper solution. Its condition also varies very considerably. Separated from weak solutions it is perfectly black and adheres firmly to the zinc, and when the solution is very weak the coating is almost impervious, the latter circumstance tending rather to the protection of the zinc than to the increase of its activity. Separated from very strong solutions, the copper is chocolate coloured or red, less adherent, and more spongy, and the crystals of the negative metal larger, which might with good reason be thought also to have an adverse influence upon the activity of the couple.

From considerations so complex as these, it became evident that the only way of arriving at a knowledge of the most effective association of the metals was by making a series of comparative trials. The experiments, the results of which are tabulated below, were therefore instituted. In each 5 meters of foil, 5 centimeters wide, weighing about 60 grams, were crumpled and cut into pieces of about 600 square millimeters. The couples were made by allowing the foil to decolorise equal volumes (450 c.c.) of copper sulphate of varying strengths, and their activity was ascertained by measuring the hydrogen evolved when placed in contact with distilled water. The action was allowed to go on for four hours before collecting the hydrogen, to allow of the hydrogenisation of the dissolved oxygen. The first reading was taken in 16 hours, the second in 40 hours.

Percentage of copper sulphate.	Copper deposited in grams.	Average Temperature.	Hydrogen evolved reduced to 0° C. and 760 mm.		Average work done by each gram of copper.		
			16 hours.	40 hours.	Between 4 and 20 hours.	Between 20 and 44 hours.	Between 4 and 44 hours.
0.55	1	17.6° C.	33.5	113.3	33.5	79.8	113.3
1.1	2	"	92.1	255.7	46.0	81.8	127.8
1.65	3	"	156.9	415.1	52.3	86.0	138.3
2.2	4	"	169.1	439.3	42.3	67.5	109.8
2.75	5	"	223.6	494.7	44.7	54.2	98.9
3.3	6	"	224.6	546.3	37.4	53.6	91.0
3.85	7	"	252.8	599.8	36.1	49.5	85.7
4.4	8	"	288.5	682.3	36.0	49.2	85.3
4.95	9	"	305.4	731.2	33.9	47.3	81.2
6.0	11	18.6° C.	352.4	889.7	32.0	48.8	80.8
7.1	13	"	389.8	988.0	29.9	46.0	76.0
8.2	15	"	468.7	1147.3	31.2	45.2	76.4
9.9	18	"	479.8	1183.7	26.6	39.0	65.7
11.5	21	"	404.8	1217.5	23.5	34.4	57.9
13.2	24	"	457.3	1161.2	19.0	29.3	48.3

These results are shown graphically on the following page :—

A represents the 4th column of the table.

B " 5th " "

C 6th

D 8th

The horizontal figures show the copper, the vertical figures being the hydrogen.

The main result of these experiments is that the action is directly proportional to the time and the amount of copper deposited; but this is modified by at least three different circumstances :—

1. The gradual oxidation of the zinc, which must necessarily diminish the action proportionally in the higher members of the series, or in the longer time.

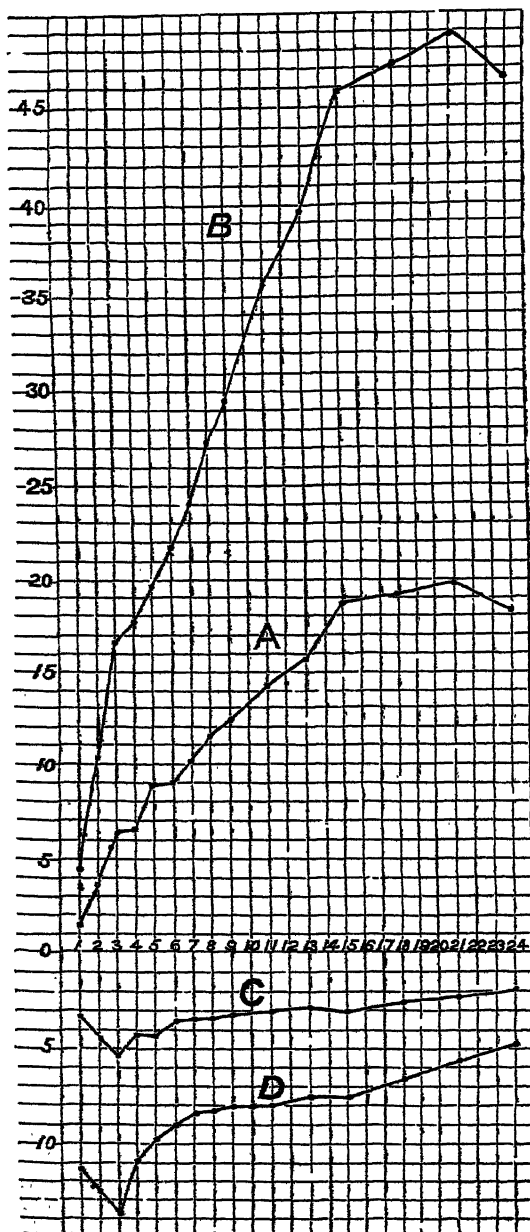
2. Something—probably the close texture of the coating—in the lower terms, which does not admit the full action to take place until we have a solution of about 1.6 per cent.

3. Something—probably the size of the base of the copper crystals—which materially interferes after about 11 per cent.

Thus, so far as this series of experiments shows, a solution of 1.6 per cent. is the most active per amount of copper deposited, and one of about 11 per cent. does the most active work.

In order to ascertain more accurately the action due to the condition and magnitude of the copper crystals, we repeated our experiments,

depositing the same amounts of copper in a series of trials, but from different strengths of copper sulphate. The particulars are given in



the subjoined table. The "number of depositions" means that one, two, &c., equal volumes of copper sulphate solution were successively decolorised.

Strength of copper sulphate.	Number of depositions.	Amount of copper in grams.	Average temperature.	Hydrogen evolved reduced to 0° C. and 760 mm.	
				16 hours.	40 hours.
11·0	1	20	17·4° C.	338·4	762·3
5·5	2	"	"	441·8	988·1
3·7	3	"	"	522·0	1124·9
5·5	1	10	"	193·9	476·5
2·7	2	"	"	244·3	573·8
1·8	3	"	"	375·9	818·6
11·0	1	20	18·5° C.	430·8	972·7
2·8	4	"	"	561·9	1335·4
1·8	6	"	"	613·4	1463·2
1·4	8	"	"	515·6	1273·4
5·5	1	10	"	300·0	730·4
1·8	3	"	"	421·4	977·0
1·4	4	"	"	468·7	1118·9
0·7	8	"	"	450·0	1095·5

A glance at the results of each of the above series of experiments confirms the conclusion previously arrived at—that the most active couple is made when the solution contains about 1·4 to 1·8 per cent. of the salt.

The practical result is, therefore, that with the zinc employed the maximum effect is produced when the 20 grams of copper are deposited from about 1·4—1·8 per cent. solution of copper sulphate in from six to eight depositions.

Assuming 1·8 as the best strength of copper sulphate to employ, it became necessary to ascertain how much copper it was desirable to deposit upon a given surface of zinc. The following series of experiments was therefore made :—

Strength of copper sulphate.	Number of depositions.	Amount of copper in grams.	Average temperature.	Hydrogen evolved, reduced to 0° C. and 760 mm.	
				16 hours.	40 hours.
1·8 per cent.	1	8·19	16·4° C.	99·1	306·3
"	2	6·38	"	226·5	591·1
"	3	9·57	"	330·4	819·1
"	4	12·76	"	382·3	914·7
"	5	15·95	"	490·8	1131·5
"	6	19·14	"	566·4	1345·7
"	7	22·33	"	612·9	1297·3
"	8	25·52	"	594·1	1334·9
"	9	28·71	"	641·2	1443·4
"	10	31·9	"	565·8	1358·5

It is evident that the activity of the couple increases with the larger amount of copper till the sixth or seventh deposition, after which there is little or no advantage.

In consequence of these experiments, and in order to avoid multiplying depositions, we have adopted, as the most convenient method of obtaining a very active couple, a solution of 2 per cent. of copper sulphate, in sufficient quantity to yield 20 grams of copper on the zinc employed.

Ethyl Hydride.

In certain reactions it is of advantage, as in the preparation of the hydrides of the alcohol-radicles, that the couple should act upon mixtures of alcohol and haloïd ethers in absence of water. All that is to be done in such cases is to wash the water couple a few times with alcohol, and add the haloïd compound alone or in admixture with alcohol. But it was necessary to ascertain whether the formula which gives a couple of maximum activity for water, would also yield the most effective couple for this class of decompositions.

Six experiments were made on the decomposition of precisely the same amounts of ethyl iodide and alcohol. The couples used were made of the same zinc foil, one-fourth of a meter in length, and were washed with alcohol. The volume of copper sulphate decolorised at each deposition measured 21 c.c., and the temperature during the experiments varied from 15—16° C. The results are given in the annexed table.

Percentage of copper sulphate.	Number of depositions.	Copper in grams.	Ethyl hydride in c.c.		
			15 mins.	1 hour.	25 hours.
2	1	·166	7*	28	514
"	2	·333	23	56	535
"	3	·499	56	—	632
"	4	·666	64	94	692
"	5	·832	71	115	722
"	6	·999	68	113	767

The augmentation of action for equal increments of copper is more rapid here than in the series of experiments with water. For practical purposes, however, it may be taken that a couple which decomposes the maximum amount of water in a given time would also yield the greatest amount of ethyl hydride by its action on a mixture of ethyl iodide and alcohol.

The time taken up in depositing a given weight of copper depends very much upon the number of depositions. With the view of ascertaining more specifically whether these could be lessened with practical advantage, we deposited the same weight of copper on equal quantities of the foil, firstly from a 6 per cent. solution in two depositions, secondly from a 2 per cent. solution in six depositions. The results were as under:—

6 per cent. solution in } two depositions .. }	Hydrogen in 16 hours, 745 c.c. " 40 " 1430 c.c.
2 per cent. solution in } six depositions }	Hydrogen in 16 hours, 878 c.c. " 40 " 1515 c.c.
6 per cent. solution in } two depositions.... }	Ethyl hydride in 1 hour, 94 c.c. " 25 hours, 620 c.c.
2 per cent. solution in } six depositions }	Ethyl hydride in 1 hour, 147 c.c. " 25 hours, 628 c.c.

It is evident that a 2 per cent. solution gives the better result.

Dry Couples.

In the preparation of certain of the organo-zinc compounds and other reactions, it is absolutely necessary to employ the couple in a dry condition. For this purpose wash the well-washed water couple with alcohol (strongly methylated), then with ether. Pour off the ether, and dry the couple in a current of hydrogen-gas,† heating the

* The solubility of ethyl hydride in the mixture doubtless affected this number.

† Hitherto we have used carbonic acid. We now recommend hydrogen or dry coal gas, because we have noticed that the couple when heated at all strongly in presence of carbonic acid, decomposes it, yielding carbonic oxide and oxide of zinc, the formation of the latter of which lessens the activity of the couple.

vessel containing it over a lamp. When the ether has escaped, heat the couple a little more strongly, keeping it gently agitated. At a certain point the couple breaks up, and becomes reduced to about a tenth of its original bulk. It should be granular and not powdery. Allow it to cool in hydrogen.

The time required to convert a given weight of ethyl iodide into zinc ethiodide (which may be taken as a typical action) by means of the dry couple, varies very much with the amount of the negative metal. The results of some of our experiments on this point are below. In each experiment half a meter of the foil was used, the volume of copper sulphate for each deposition being 42 c.c. The flasks containing the couples and 5 c.c. of ethyl iodide were attached to an inverted condenser, and heated by immersion in boiling water. As soon as the dropping ceased from the condenser, the conversion was deemed complete.

Percentage of copper sulphate.	Number of depositions.	Copper deposited in grams.	Time for conversion into ethiodide in minutes.
1*	1	0.083	14 minutes.
1	2	0.333	12.5 and 14
2	1	0.333	6 and 9
2	2	0.666	9
2	4	1.333	26

Here it is seen that one deposition from a 2 per cent. solution of copper sulphate gives a dry couple of maximum activity. The weight of zinc used to the copper is in the ratio of 1 : 0.036. The reason why so small a quantity of the negative metal produces the best result, is not difficult to give. On drying, the projecting copper crystals doubtless, when of any length, undergo disintegration, thereby breaking metallic contact with the zinc. The bases, however, of these crystals adhere firmly, and this is probably the only portion of the deposited copper which assists in the action.

The quantity of gaseous hydrocarbons produced in the first three of the above experiments was nearly the same, measuring 4.7 c.c., which means a loss of about 0.03 gram of ethyl iodide out of 9 grams. To obtain a knowledge of the actual advantage of the couple, an experiment was made as follows. Half a meter of the zinc foil was crumpled and cut into small pieces, washed with alcohol and ether, and reduced while hot by agitation to about the same bulk as were the couples. The time required to convert 5 c.c. (9.5 grams) of ethyl

* Only half the volume was used in this experiment.

iodide at about 100° C., was about 3 hours and 20 minutes, and the amount of hydrocarbons collected measured 164 c.c., which means a loss of 1.14 gram of the iodide. Thus zinc containing about 1 per cent. of the negative metal lead, takes 26.5 times as long in doing the same work as does the dry couple, and causes 34.5 times the loss by destroying the substance it is desirable to conserve.

Were pure zinc employed, the difference would doubtless be even more strongly marked, because after the surface of the zinc has been slightly corroded, any lead present as an impurity must act, to a greater or less extent, the part of the copper in our couple. This supposition was subsequently confirmed by the following experiment:—

Some zinc was reduced by ourselves, starting with pure sulphate, and without touching anything but porcelain. A quantity of this zinc was granulated, and the finer portions were picked out. 10.31 grams were heated for $6\frac{1}{2}$ hours with 5 c.c. of ethyl iodide. The flask was then washed out with anhydrous ether, water was added, the solution evaporated, and the zinc in solution determined. Zinc oxide found 0.0051 gram. The same zinc was then coupleised, and heated with the same amount of ethyl iodide. In 3 hours 25 minutes, the action was over, the flask was washed out with ether, the solution added to water, and precipitated by sodium carbonate. Zinc oxide found = 2.692 grams. These data give for equal times an amount of action 1004 times greater in the case of the couple than in the case of pure zinc.

In the conversion of ethyl iodide into the ethiodide on a larger scale, the temperature rises so quickly as frequently to necessitate the application of cold water to the flask. We have noticed that the mere heating of the ethiodide to 100° C. slowly evolves hydrocarbons. To prevent loss therefore, the conversion should be got over as quickly as possible. We have noticed too, that sometimes a small quantity of free zinc-ethyl in addition to the ethiodide is formed in the reaction, especially when it is carried on on a large scale, which flowing down the inner tube of the condenser, may give the impression of the non-conversion of the whole of the iodide.

We do not recommend granulated zinc for larger operations, from the impracticability of ascertaining the surface of any given weight of it; but we see no reason why the ordinary thin sheet zinc of commerce should not be used, which would avoid the employment of the more expensive foil.

In an experiment employing 4 meters of foil coated with 6.72 grams of copper deposited from a 2 per cent. solution of copper sulphate, and 60 c.c. of ethyl iodide (115 grams), we obtained within two hours, which includes the preparation of the couple, the conversion

into ethiodide, and subsequent distillation, 40 grams of perfectly clear zinc-ethyl, or 88·4 per cent. of the theoretical quantity, which is 18·7 per cent. in excess of what we obtained in the best operation, on one-twelfth the scale, described in our original paper on this subject.

The following are the recommendations, relative to the best proportions of zinc, and the strength and quantity of the copper sulphate to be employed in the preparation of copper-zinc couples, based on our results.

Dry Couples.—Add 84 c.c. of a 2 per cent. solution of anhydrous copper sulphate to 1 meter of foil 5 centimeters wide, that is 500 square centimeters, exposing on the two sides a surface of 1000 square centimeters, crumpled as directed.

Couples wet with Alcohol or Water.—To 1 meter of the same foil, add 84 c.c. of a 2 per cent. solution of the sulphate, allow the solution to decolorise, pour off the zinc sulphate, and repeat five times.

We would now draw attention to a few points which appear of special interest in connection with the action of the couple.

It is known that zinc does not decompose liquid water at any temperature at the ordinary pressure, but that the couple does even at as low a temperature as 2° C. It is known also that water is electrolyzed by a small battery power. Again, zinc at the ordinary temperature has no action upon a mixture of ethyl iodide and alcohol, whereas the couple decomposes it readily. Yet no signs of electrolysis could be detected when this mixture was submitted to the action of 100 Grove's cells, even when the platinum electrodes employed were very close together.

It would appear then that this simple association of metals is more powerful for effecting the decomposition of certain organic bodies, than the electric power derivable from a large battery.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Selective Absorption. By W. ACKROYD (*Phil. Mag.* [5] ii, 423—430).—Two classes of absorption-spectra exist, which should be clearly differentiated from each other. The one depends upon an alteration of the molecular *arrangement* of the substance producing absorption; the other upon the *extent* of absorbing substance through which the ray passes. Thus the absorptive power of a section of potassium dichromate is increased by heating the crystal, and in like manner the absorption produced by a solution of copper sulphate is increased by passing the ray through a greater thickness of liquid. The former is sometimes called *structural* absorption; the latter, *transverse* absorption.

Alteration of structural absorption on elevation of temperature is often rendered obvious to the eye by a change of colour, as when zinc oxide, lead chromate, or mercuric oxide is heated; and a study of the chromatic effects produced by these and similar substances, has led to the observation of the following sequence in order of colour.

Metachromatic Scale.—White or colourless, blue, green, yellow, orange, red, brown, black. Thus zinc oxide changes from white to yellow and orange; copper metaborate from blue to green and yellowish-green; barium chromate from yellow to orange; mercuric oxide from orange-yellow to orange, red, and brown; potassium dichromate, red to dark-red; trimanganic tetroxide, reddish-brown to nearly black; and cuprous oxide glass from scarlet to dark scarlet and black.

Respecting this colour change, the author considers (1) that it arises from internal structural absorption; (2) that the change from the white in the direction of the black end of the scale signifies atomic recession, and a change in the opposite direction atomic approach. That when a body is heated it acquires an accession of energy, a portion of which being transformed into energy of position becomes evident to the senses, first in the weakening of cohesion or molecular union, and afterwards in the more complete disruption of atomic combination.

Change of colour denoting increase of kinetic energy does not always carry with it increase of structural absorption, since the absorptive power of mercuric iodide diminishes on heating; moreover there seems to be sometimes a change of colour, as in the beryl, without alteration of density, *i.e.*, without appreciable molecular approach or recession, and sometimes a change of density (molecular recession) as in olivine, without a corresponding alteration of colour, from which it must be inferred that molecular expansion or contraction is not a

necessary concomitant of alteration of structural absorption, although probably there is always more or less tendency to overcome chemical attraction, and to resolve the compound into simpler substances or into its constituent elements.

The author alludes briefly to the relation of colour to density, and to the five orders of spectra as proposed by Lockyer. With respect to the latter he thinks that in the light of meta-chromatism it may be necessary to modify the generally accepted sequence, since the fifth order—unique continuous absorption—is from the nature of the experiment a *transverse* absorptional effect, whereas with absorption spectra at least, the only data available for forming a sequence of orders are observations respecting change in *structural* absorption.

J. W.

Alkaline Development of the Photographic Image. By Captain ABNEY (*Phil. Mag.* [5], iii, 46—51).—The action of the alkaline developer now used in photography, which consists of a solution of pyrogalllic acid, potassium or ammonium hydrate, and potassium bromide, not being clearly understood, the following experiments were undertaken in order to throw if possible greater light upon the subject.

A bulb was blown at both ends of a glass tube; the tube was bent after the manner of a differential thermometer, and was provided with a lateral branch by which it could be attached to a Sprengel pump, and through which materials could be introduced. In one bulb, carefully excluded from light, silver bromide and pyrogalllic acid were placed; in the other, solution of caustic potash; the apparatus was then exhausted and sealed. The contents of the bulbs were mixed, allowed to react from 2 to 60 hours, and then analysed. In this manner it was ascertained (i) that the pyrogalllic acid was without action on silver bromide, unless an alkali was present; (ii) that the bromide was instantly attacked by the alkaline pyrogallate without exposure to light; (iii) that the extent of reduction depended partly upon the amount of pyrogalllic acid present, and partly upon the amount of alkali; (iv) that the reduction was independent of absorption of atmospheric oxygen.

When a considerable proportion of potassium bromide was added to the alkali, the same results were obtained, but the reduction of the silver bromide was effected more slowly. This important restraining action of the soluble bromide was proved by several distinct experiments. In order to ascertain the means by which the density in an alkaline-developed image was produced, a plate prepared with silver iodide (which is not amenable to alkaline development) was covered with a solution of tannin in dilute albumin and dried. After exposure in the camera, one-half of it was coated with an emulsion of silver bromide in collodion. On developing, a clear distinct image gradually appeared upon that portion of the plate only which had been treated with silver bromide. Owing to the solubility of silver bromide in ammonia, when that alkali was used in the developing solution, the image was on the exposed film, but when caustic potash was substituted, the image was on the top unexposed film. It was, however, distinctly proved that the photographic image had no power of trans-

ferring itself or of creating a sympathetic action in an unexposed film previous to development, by achieving the rather difficult experiment of separating the two films and developing them separately; when this was successfully accomplished, no image was ever obtained on the unexposed film.

The formation of a secondary image, which takes place when a picture is "intensified," that is, when the opacity of its reduced portions is increased, cannot be said to have been yet satisfactorily explained.

J. W.

Researches on the Coefficient of Capillarity. By AUG. GUEROUT (*Compt. rend.*, lxxxiii, 1291).—The author finds that in any series of organic compounds the coefficient of capillarity decreases as the quantity of carbon increases. This observation was proved on three series, namely, the fatty acids, the acid ethers of the same alcohol, and the ethers formed by the union of the same organic acid with the different fatty alcohols.

The following tables contain the numbers obtained at a temperature of 15° C. :—

Acids.

	Coefficients.
Formic acid (CH_2O_2)	115.0
Acetic acid ($\text{C}_2\text{H}_4\text{O}_2$)	160.5
Propionic acid ($\text{C}_3\text{H}_6\text{O}_2$)	189.0
Butyric acid ($\text{C}_4\text{H}_8\text{O}_2$)	129.5
Valerianic acid ($\text{C}_5\text{H}_{10}\text{O}_2$)	92.3
Caproic acid ($\text{C}_6\text{H}_{12}\text{O}_2$)	64.0

Ethers.

1st Series.	Coefficients.
Ethyl formate ($\text{C}_3\text{H}_6\text{O}_2$)	542.0
Ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$)	450.3
Ethyl propionate ($\text{C}_5\text{H}_{10}\text{O}_2$)	360.3
Ethyl butyrate ($\text{C}_6\text{H}_{12}\text{O}_2$)	297.0
Ethyl valerate ($\text{C}_7\text{H}_{14}\text{O}_2$)	241.3
2nd Series.	Coefficients.
Methyl acetate ($\text{C}_3\text{H}_6\text{O}_2$)	534.5
Ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$)	450.3
Propyl acetate ($\text{C}_5\text{H}_{10}\text{O}_2$)	362.8
Butyl acetate ($\text{C}_6\text{H}_{12}\text{O}_2$)	305.3
Amyl acetate ($\text{C}_7\text{H}_{14}\text{O}_2$)	230.2

On examining the numbers, it may be seen that the acids, after propionic acid, agree with the law above stated. Acetic and formic acids are the only exceptions, a fact possibly due to impurities in the specimens examined.

The two series of ethers agree perfectly with the law.

It is also apparent that the coefficient of capillarity of the ethers is much higher than that of the alcohols or acids which give rise to them,

i.e., the introduction of an organic radicle into the molecule of an alcohol increases the fluidity of the body.

If the two series of ethers be compared, it is seen that the isomeric ethers have nearly the same fluidity, whereas the acids isomeric with them are far inferior in that respect. Thus ethyl propionate and propyl acetate have the coefficients 360.3 and 362.8 respectively; while valeric acid, which is isomeric with them, has the coefficient 92.3, only about one-quarter as great.

The reason of this is, doubtless, that in the two isomeric ethers the atoms are grouped in a similar way, while in the isomeric acids the grouping is totally different.

C. W. W.

Thermo-Chemical Researches. By JULIUS THOMSEN (*J. pr. Chem.* [2], xiv, 413—442).—*Nickel and Cobalt.* These metals in their dynamical relations stand nearest to iron, the order of affinity being Fe—Co—Ni. The heat of formation of the monoxides, sesquioxides and anhydrous chlorides is shown in the following table:—

R.	($R.O.H_2O$)	($R_2O_3.3H_2O$)	(RCl_2)
Fe	68280 heat-units.	191130 units.	82050 units.
Co	63400 "	149300 "	76480 "
Ni	60840 "	120380 "	74530 "

The analogy of the three metals is shown by their heat of neutralisation, and the evolution of heat on solution of the anhydrous chlorides in water—

R.	($\overline{R}.SO_3Aq.$)	($\overline{R}.2HClAq.$)	($RCl_2.Aq.$)
Fe.....	24920 units.	21390 units.	17900 units.
Co.....	24670 "	21140 "	18340 "
Ni.....	26110 "	22580 "	19170 "

The difference between the three is shown by the evolution of heat on formation of the sesquioxides from the protoxides—

R.	($2RO_2.H_2O.H_2O$)
Fe	54570 heat-units.
Co	22500 "
Ni	— 1300 "

It is owing to this difference that iron sesquioxide dissolves in dilute sulphuric acid without decomposition, whilst cobalt sesquioxide gives off oxygen, with formation of a cobaltous salt, and in the case of nickel the decomposition is very energetic. For the same reason the acid solutions of nickel and cobalt sulphates are not oxidised in the air. On the other hand, the free monoxides, or their ammoniacal solutions behave quite differently—the oxidation of iron monoxide being represented by 54570 heat-units, that of cobalt monoxide by 22500 units, whilst nickel monoxide with the negative quantity of — 1300 units remains unaltered.

Nickel and cobalt decompose water—they dissolve in dilute acids with evolution of hydrogen. In this respect they stand between

cadmium and tin as is shown by the evolution of heat on decomposition of dilute hydrochloric acid by these metals thus :—

Zinc	34200 heat-units
Iron	21310 "
Cadmium	17610 "
Cobalt	16180 "
Nickel	15060 "
Tin	2500 "

The following table gives the values determined for cobalt and nickel. Ni and Co = 59. Temperature = 18° :—

Reaction.	Evolution of Heat.	Explanation.
Co.Cl ₂	76480 heat-units.	Anhydrous chloride
Co.O.H ₂ O.....	68400 "	{ Monoxide and hydrated oxide from metal, oxygen, and water
Co ₂ .O ₃ .3H ₂ O	149300 "	
Co.O ₂ SO ₂ .7H ₂ O..	162970 "	Crystallised sulphate
2CoO ₂ H ₂ .O.H ₂ O .	22500 "	{ Oxidation of monoxide to sesquioxide .
2Co ₂ O ₃ H ₂ .O.H ₂ O .	— 700 "	
CoO ₂ H ₂ .2HClAq.	21140 "	{ Further oxidation of sesquioxide Heat of neutralisation of mon- oxide.
CoO ₂ H ₂ .SO ₃ Aq	24670 "	
CoCl ₂ .Aq.	18340 "	{ Heat of solution of anhydrous chloride, and crystallised sul- phate
CoSO ₄ .7H ₂ OAq..	—3570 "	
Co.Cl ₂ .Aq.....	94820 "	{ Formation of chloride and sul- phate in aqueous solution
Co.O.SO ₃ Aq.....	88070 "	
Ni.Cl ₂	74580 "	{ Anhydrous chloride Monoxide and sesquioxide
Ni.O.H ₂ O	60840 "	
Ni ₂ .O ₃ .3H ₂ O	120380 "	{ Crystallised sulphate Oxidation of monoxide to sesquioxide
Ni ₂ .O ₂ .SO ₂ .7H ₂ O.	162530 "	
2NiO ₂ H ₂ .O.H ₂ O..	—1300 "	{ Heat of neutralisation Heat of solution of anhydrous chloride and crystallised sul- phate
NiO ₂ H ₂ .2HClAq.	22580 "	
NiO ₂ H ₂ .SO ₃ Aq. .	26110 "	{ Formation of chloride and sul- phate in aqueous solution
NiCl ₂ .Aq.	19170 "	
NiSO ₄ .7H ₂ OAq...	—4250 "	
Ni.Cl ₂ .Aq.	93700 "	
Ni.O.SO ₃ Aq.	86950 "	

Tin. Sn = 118. Temperature 18°.

Evolution of Heat on Solution of Compounds in Water.

Reaction.	Evolution of heat.	Explanation.
SnCl ₄ .Aq.	29920 heat-units.	Anhydrous tetrachloride
SnCl ₄ K ₂ .Aq.	—3380 "	Chloride of tin and potassium
SnCl ₂ .Aq.	+ 350 "	Anhydrous dichloride
SnCl ₂ .2H ₂ O.Aq...	—5370 "	Crystalline hydrated dichlor- ide

Heat of Formation of the Chlorides and Oxides of Tin.

Reaction.	Evolution of heat.	Explanation.
Sn.Cl_2	80790 heat-units.	Formation of anhydrous chlorides from metal and chlorine
Sn.Cl_4	127240 "	
$\text{Sn.O.H}_2\text{O}$	68090 "	Formation of hydrates from metal, oxygen, and water
$\text{Sn.O}_2.2\text{H}_2\text{O}$	133490 "	
$\text{SnCl}_2.2\text{H}_2\text{O}$	5720 "	Crystalline hydrated protochloride
$\text{SnCl}_4.2\text{KCl}$	24160	Crystalline chloride of tin and potassium
$\text{SnO}_2.\text{H}_2.2\text{HClAq.}$..	2770	Heat of neutralisation of oxides for hydrochloric acid
$\text{SnO}_2.\text{H}_2.4\text{HClAq.}$..	3110	
$\text{SnO}_2.\text{H}_2.2\text{NaOHAq.}$..	215	Heat of neutralisation of oxides for sodium hydrate
$\text{SnO}_2.\text{H}_2.4\text{NaOHAq.}$..	9560	
$\text{Sn.Cl}_2.\text{Aq.}$	81140	Aqueous solutions of chlorides from metal, chlorine, and water
$\text{Sn.Cl}_4.\text{Aq.}$	157160	
$\text{SnCl}_4.\text{Aq.} . 2\text{KClAq.}$..	-250	Reaction of tin tetrachloride on potassium chloride in aqueous solution

The affinity of tin for both oxygen and chlorine is very great, but more so for the latter than the former body. The formation of the hydrated oxide of tin from the metal, oxygen and water is accompanied by the same evolution of heat as the formation of hydrated monoxide of iron, and of water, thus:—

$$\text{Sn.O.H}_2\text{O} = 68090 \text{ heat units}$$

$$\text{Fe.O.H}_2\text{O} = 68280 \quad "$$

$$\text{H}_2\text{O} = 68360 \quad "$$

The affinity of tin for oxygen is 2410 heat-units greater than that of cadmium, but 14590 less than that of zinc.

Tin readily takes up another atom of oxygen, and the oxidation of the hydrated monoxide into the hydrated dioxide is accompanied by an evolution of 65400 heat-units.

The heat of neutralisation of the monoxide of tin for hydrochloric acid is 2770 heat-units, that of the dioxide for soda 9560 heat-units. Hence tin does not readily decompose water either in weakly acid or in alkaline solutions. The reduction of water by tin and very dilute hydrochloric acid, gives only 2500 heat-units; but the evolution of heat and rapidity of decomposition increase with the degree of concentration of the acid. This is the reason why tin is a suitable reducing agent for many organic bodies, since the oxidation of the tin takes place at the cost of the more easily reducible body. The heat of formation of the anhydrous stannous chloride is almost the same as that of ferrous chloride, mercurous chloride, and lead chloride.

$$\text{Sn.Cl}_2 = 80790 \text{ heat-units}$$

$$\text{Fe.Cl}_2 = 82050 \quad "$$

$$\text{Hg}_2.\text{Cl}_2 = 82550 \quad "$$

$$\text{Pb.Cl}_2 = 82770 \quad "$$

On the other hand the behaviour of these chlorine compounds to water is very different, the evolution of heat on solution of stannous chloride being +350 units, ferrous chloride +17900 units, lead chloride -6800 units, that of mercurous chloride is unknown.

A comparison of the higher chlorides of these metals gives—

Fe_2Cl_6	$= 192060 = 3.64020$	heat-units
SnCl_4	$= 127240 = 2.63620$	"
HgCl_2	$= 63160 = 1.63160$	"

But as the number of chlorine molecules in the compound is as 3 : 2 : 1, it follows that the formation of ferric, stannic and mercuric chlorides is accompanied by an equal evolution of heat for equal quantities of chlorine. The protochlorides therefore of iron, tin, and mercury are formed with the evolution of the same quantity of heat, amounting in the mean to 81800 units for each molecule of chlorine, and the perchlorides also show an equal evolution of heat amounting to 63600 units for each molecule of chlorine. One may therefore suppose that the union of the chlorine atoms in the perchloride is of a similar nature, and that the perchloride is not made up of the protochloride and chlorine.

The chlorine in these dichlorides corresponds with an evolution of 81800 units of heat, and in the tetrachlorides with 63600 units per molecule, and the difference of these values 18200 units is the quantity which the author has often pointed to as the thermo-chemical constant.

Again, $81800 = 9.9089$
 $63600 = 7.9086,$

thus the absolute evolution of heat for chlorine in the two groups shows the same constant for half of $18200 = 9100$.

Whether other metals which have more than one chloride exhibit the same relation is not known, since those of copper only have been investigated.

The evolution of heat for cuprous chloride is 65750, for cupric chloride 51630 heat-units for each molecule of chlorine: the absolute evolution of heat is therefore considerably less than in the above cases; but—

$$\begin{aligned} 81800 : 63600 &= 1.286 : 1 \\ 65750 : 51630 &= 1.274 : 1, \end{aligned}$$

and therefore the quantities of heat evolved by cuprous and cupric chloride stand in the same relation as those of the lower and higher chlorides of tin, iron, and mercury.

G. T. A.

Inorganic Chemistry.

Decomposition of a Solution of Potassium Iodide by Light.
 By BATTANDIER (*J. Pharm. Chim.* [4], xxiv, 209—214).—Many chemists have noticed that a solution of potassium iodide under the

influence of sun-light becomes rapidly yellow, and after a short time is found to contain free iodine. Vidau (*J. Pharm. Chim.*, 1874) states that this decomposition is due to the action of light alone without the intervention of air, and to test the truth of this the author carried out the experiments described in this paper. He exposed a solution of potassium iodide: 1st, to sun-light and air; 2nd, to sun-light in a vacuum; 3rd, to air in the shade.

The decomposition took place in the first case only, and the experiments were repeated three times with the same result. It must therefore be admitted that air is necessary to the decomposition.

Solutions of potassium iodide were also placed under the following conditions:—

- 1st. Exposed to air and sun-light.
- 2nd. Exposed to air and sun-light after boiling.
- 3rd. Exposed to air and sun-light after a current of carbonic acid gas had been passed through it.
- 4th. Mixed with a little barium chloride and exposed to air and light.
- 5th. Mixed with a little caustic potash, and exposed to air and light.
- 6th. Exposed to sun-light in air free from carbonic acid.
- 7th. Placed in carbonic acid gas and exposed to sun-light.

In experiments 4, 5, and 6, there was no appreciable decomposition. In experiment 7, on the contrary, it was so energetic that in two hours the solution was decidedly yellow, and became gradually darker. In experiment 3 the decomposition was less energetic; still less in experiment 1, and less again in experiment 2.

The author concludes that sun-light and the acids of the air, more especially carbonic acid, are the principal causes of the change. He considers it probable that it results from the disengagement of a small quantity of hydriodic acid.

H. H. B. S.

Action of Phosphorus on Iodates in Presence of Atmospheric Oxygen. By I. CORNE (*J. Pharm. Chim.* [4], xxiv, 216—218).—In a former paper the author showed that the reduction of iodine observed on placing a piece of phosphorus in contact with a solution of an iodate was due not to the action of the phosphorus itself, but to the acid formed by its oxidation. This having since been disputed by Pollacci (*J. Pharm. Chim.* [4], xxiii, 178; *J. Chem. Soc.*, 1877, vol. i, 344), fresh experiments were made, the results of which corroborate the author's former statement. He concludes that—

1. Phosphorus itself has absolutely no action upon the iodates.
2. The reduction in question is dependent upon the oxidation of the phosphorus.

H. H. B. S.

Precipitation of Phosphoric Acid by Ammonia in presence of Lime, Baryta, Magnesia, Alumina, and Ferric Oxide. By H. PELLET (*Bull. Soc. Chim.* [2], xxvii, 105).—A solution was prepared containing 1 grm. of phosphoric acid, baryta sufficient to saturate it, and some lime, but not enough to form tricalcic phosphate with the phosphoric acid. On adding ammonia, the whole of the

lime was precipitated as tribasic phosphate, the excess of phosphoric acid combining with baryta.

When magnesia was substituted for lime, ammonia precipitated first $P_2O_5 \cdot 2MgO \cdot H_2O$, and then baric phosphate.

With an insufficient quantity of lime and an excess of magnesia, ammonia precipitated phosphate of lime, the excess of phosphoric acid combining with magnesia. From a solution containing 3 parts of P_2O_5 , sufficient lime to saturate $\frac{2}{3}$ th of this, magnesia to saturate $\frac{1}{3}$ th, and baryta in excess, ammonia precipitated all the lime as $P_2O_5 \cdot 3CaO$, the magnesia combining with phosphoric acid to form $P_2O_5 \cdot 2MgO \cdot H_2O$, and the excess of phosphoric acid with baryta to form barium phosphate.

If a solution contain phosphoric acid, besides lime, baryta, magnesia, alumina, and ferric oxide, each in sufficient quantity to saturate it, the addition of ammonia causes the precipitation of tricalcic phosphate, alumina, and ferric oxide.

In conclusion, the addition of ammonia to a solution containing phosphoric acid, lime, baryta, magnesia, alumina, and iron, produces a precipitate composed of, 1st, $P_2O_5 \cdot 3CaO + Al_2O_3 + Fe_2O_3$, if there is sufficient lime to combine all the phosphoric acid; secondly, of $P_2O_5 \cdot 3CaO + P_2O_5 \cdot 2MgO \cdot H_2O + Al_2O_3 + Fe_2O_3$, if there is only sufficient lime to saturate a part of the phosphoric acid; or 3rd, of $P_2O_5 \cdot 3CaO + P_2O_5 \cdot 2MgO \cdot H_2O + P_2O_5 \cdot 3BaO + Al_2O_3 + Fe_2O_3$, if the lime and magnesia together are not sufficient to saturate the phosphoric acid.

H. H. B. S.

Mutual Action of Potassium Iodide and Lead Sulphate. By G. CAMPANI (*Gazzetta chimica italiana*, vi, 461—464).—The author finds that when lead sulphate and potassium iodide in molecular proportions are treated with water at the ordinary temperature, a large portion of the lead salt is converted into iodide, which may then be dissolved out by treatment with boiling water. With the above proportions, this product amounts to 36.5 per cent. of the whole; but if 4 mols. of potassium iodide be employed, as much as 73.6 per cent. is converted at the ordinary temperature, and 76 at 130°. In the latter case the colourless needles of the double iodide of lead and potassium described by Boullay were produced. Lead phosphate is similarly acted on by potassium iodide; so that this property forms a means of detecting lead in toxicological investigations; after incineration, the residue, which is insoluble in water, and contains the lead as sulphate and phosphate, becomes yellow when moistened with a solution of potassium iodide.

C. E. G.

Glucinum: its Atomic Weight and Specific Heat. By J. EMERSON-REYNOLDS (*Phil. Mag.* [5], iii, 38—42).—From three kilograms of crude Irish beryls about 350 grams of pure glucinum oxide were obtained. The oxide was converted into the anhydrous chloride, and the metal obtained therefrom by the action of sodium; the reduced glucinum was finally brought into a coherent mass by fusing it under common salt in a lime crucible. The apparatus used for determining the specific heat was constructed after the pattern of

Bunsen's ice-calorimeter, which, however, it resembled in form rather than in principle, since the readings depended upon the expansion of alcohol. The lower portion of the apparatus, as in Bunsen's arrangement, was filled with mercury, and connected with a capillary tube so as to form a scale; the space above immediately surrounding the interior tube was filled with alcohol. One cubic centimeter of distilled water having been placed in the inner tube, and the temperature having been equalised, the graduation of the mercurial scale was effected by dropping into the tube 108 centigrams of pure silver heated to 100° . The expansion caused in a given time was noted, and a measure of the atomic heat in terms of the graduation thus obtained. Assuming 9.2 to be the atomic weight of glucinum, the experimental number obtained for its atomic heat was 5.91, which gives 0.642 for its specific heat. Taking the atomic heat of silver 6.157 as the constant, the specific heat calculates as follows:—

Atomic weight	=	4.6	1.338	=	sp. heat.
"	=	9.2	0.669	=	"
"	=	13.8	0.446	=	"

The atomic weight of glucinum is therefore about 9.2, so that the formula of its chloride will be RCl_2 .

A new determination of the equivalent is in progress.

J. W.

Mineralogical Chemistry.

Ludlamite, a New Cornish Mineral. By FREDERICK FIELD (*Phil. Mag.* [5], iii, 52—57).—Ludlamite is a hydrated basic ferrous phosphate, found associated with quartz, chalybite, vivianite, iron pyrites, and mispickel. Hardness = 3.4; specific gravity = 3.12. Colour, clear green, from pale to dark, transparent and brilliant. Streak very pale green, approaching to white. It tinges the flame of the blowpipe slightly green, and yields a semi-fused blackish residue. It is soluble in dilute mineral acids, and is readily decomposed by boiling with a solution of caustic alkali. The results of analysis are as follows:—

Fe.	P_2O_5 .	H_2O .
52.76	30.11	16.98 = 99.85.

These numbers correspond very closely with the formula $7\text{FeO} \cdot 2\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$. The mineral differs from vivianite ($3\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$) in the fact that it decrepitates violently when heated, and breaks up into brilliant crystalline plates of an intense bluish-green colour. Vivianite, on the contrary, does not decrepitate, but gradually exfoliates and turns white.

The crystallographic relations of the mineral are given in the original communication.

J. W.

Nickel Ores. By H. LASPEYRES (*J. pr. Chem.* [2], xiv, 397—413).—*Polydymite*—a New Nickel Ore.—This mineral consists of fine grey twin octohedral crystals, which decrepitate strongly before the blowpipe. When they are strongly heated, a yellowish sublimate of sulphur and minute traces of a yellowish-brown sublimate of sulphide of arsenic are deposited in the tube. The residue fuses upon charcoal to a dark green magnetic bead, with a crystalline fracture of a yellowish colour, while very minute traces of antimony are volatilised. With borax and microcosmic salt, the reactions of nickel and iron are produced, but scarcely any trace of cobalt can be detected. The mineral is soluble in nitric acid, with separation of sulphur, and the solution, when cooled and diluted, is of a clear green colour, which becomes blue on addition of excess of ammonia, though only a very little iron is precipitated. It is perfectly insoluble in strong hydrochloric acid. The empirical formula of polydymite is R_4S_8 , and its percentage composition Ni. 59.447; S. 40.553. A small part of the nickel may be replaced by iron. Polydymite does not seem to be the same as beyrichite found in the same locality, though it may possibly be shown to be a variety of cobalt-nickel pyrites, containing only a trace of cobalt.

Saynite.—The mineral hitherto known by this name, or nickel-bismuth glance, is essentially a mixture of polydymite with bismuth glance. G. T. A.

New Minerals from the Graphite Deposits of Mugrau. By A. SCHRAUF (*Chem. Centralb.*, 1876, 231).—One of these minerals found by the author last year in the south of the Bohemian forest was named *Ihleite*. Its formula is $Fe_2S_3O_{12} + 12H_2O$; it occurs as a yellow efflorescence on graphite. He also found crystals of *calcite* on quartz resembling chrysoprase in appearance, as well as yellow chloropal. He also mentions a specimen of *analcite*, in which twin crystals were developed, the angle between the surfaces of two cubes being 89.30° . The difference between this irregularity from the monometric system and that of leucite is much less in the former instance. Brewster had already remarked the different optical behaviour of analcite from that of singly refracting bodies. W. R.

On some Minerals from the Silurian Iron-stone Deposits, and the Coal-formation of Bohemia, resembling Ankerite; and on the Chemical Constitution of the Minerals classed with Ankerite. By E. BORICKY (*Jahrb. f. Min.*, 1876, 560—561).—Under the name of ankerite there is a group of carbonates which approach very nearly to bitterspar, differing in respect of their high percentage of ferrous carbonate. Their general chemical formula is $\begin{cases} CaFeC_2O_6 \\ xCaMgC_2O_6 \end{cases}$, x having ten different values. The values for x in the first five combinations are given by the author as: $x = \frac{1}{2}, 1, \frac{2}{3}, \frac{3}{4}, \frac{4}{5}$ for *ankerite*, the remaining values to *parankerite*, normal ankerite having the formula $\begin{cases} CaFeC_2O_6 \\ CaMgC_2O_6 \end{cases}$; and normal *parankerite* $\begin{cases} CaFeC_2O_6 \\ 2CaMgC_2O_6 \end{cases}$. The intermediate numbers of the group are distinguished by Greek letters.

Normal ankerite occurs at Gifberg near Kommoran, at Zajecow in Bohemia and Lobenstein, and at Kall in the Eifel; Normal parankerite occurs at Rapic near Kladno; at Lubna near Rakonitz; at Schwadewitz Ploskow near Lalma, &c., in Bohemia; at Cornighon near Vizille in France; and in Nova Scotia. C. A. B.

Gypsum Crystals from Sütel. By PAUL KLEIN (*Jahrb. f. Min.*, 1876, 556—557).—Gypsum crystals are abundant in the miocene clay of Sütel in Holstein. The usual forms occur here, but occasionally curious groups are found which bear a resemblance to twins, but are not so in reality. One crystal in these groups is larger in size than any of the rest, and at the same time serves as a support for the other crystals, which seem to radiate outwards from its centre. These crystals mostly enclose ferric oxide, which is distributed parallel to the various crystal faces, often assuming the appearance of a kernel in the crystal enveloped by ferric oxide. Sometimes this deposition is repeated, giving rise to the formation of parallel zones.

The Crystal-tectonic of Gypsum (*Jahrb. f. Min.*, 1876, 563).—The author examined the connection existing between the enclosures of gypsum crystals and their structure. The result of his labours is briefly as follows:—"The arrangement of the sub-individuals of gypsum occurs in the clinopinacoid as principal tectonic plane, the vertical axis and parallel an edge of coP being the principal zonal-axes. The principal zones of gypsum coincide with the tectonic axes."

C. A. B.

The Stilbite (Desmine) of Nova Scotia. By H. How (*Jahrb. f. Min.*, 1876, 559).—This mineral occurs in most beautiful crystals of a honey-yellow colour in amygdaloid at Partridge Island; in radiating semi-globular masses at Margaretville and Hall's Harbour; also in groups of long, broad prismatic colourless, and brown crystals, and in veins several inches thick. Stilbite from this country having never before been analysed, the author submitted a fine specimen of a milk-white colour to analysis and found it to have the following composition:—

SiO_2 .	Al_2O_3 .	CaO .	Na_2O .	H_2O .
57.32	17.28	7.57	2.10	16.52 = 100.76

C. A. B.

Staurolite Crystals from Fannin, Georgia. By ED. DANA (*Jahrb. f. Min.*, 1876, 555).—These crystals, found in a metamorphic schist of the Cincinnati group, were nearly one inch in length and almost always twins. They were characterised by a peculiar hemihedry, viz., an opposite pair of faces of $P\bar{o}$ was absent, whilst the remaining pair was much developed. The prism also exhibited this peculiar hemihedral development, causing the crystals to appear oblique. Twins were found occurring according to a new law for this mineral, viz., the twin plane a face of $coP\bar{3}$. A trilling was found exhibiting both the usual twin laws for this mineral together.

C. A. B.

A Twin Crystal of Pyrrhotin. By ED. DANA (*Jahrb. f. Min.*, 1876, 557—558).—The vertical crystal of this twin exhibited the combination of the hexagonal pyramid with the basal terminal plane. The pyramidal faces were strongly horizontally striated and exhibited numerous indentations parallel to the vertical axis. The other individual of this twin was built up irregularly out of a group of numerous small parallel-lying crystals, which proved to be the pyramid $\frac{2}{3}P$, the lateral edge angle measuring 163° ; twin plane a face of P . An analysis of a crystal gave the following result:—

Fe.	Cu.	Mn.	Ni.	Co.	S.	SiO ₂ .
60.560	0.145	0.060	0.112	0.111	39.020	0.336 = 100.344

Specific gravity 4.622. Pyrrhotin is found generally in good crystals, more rarely massive, in a bed of iron-pyrites in Laurentian rocks, near Elizabeth Town, Ontario. C. A. B.

Bourmonite from Waldenstein, Carinthia. By V. v. ZEPHAROVICH (*Jahrb. f. Min.*, 1876, 555—556).—Some specimens from this locality exhibited the following forms:— $0P$, $\infty P\bar{\infty}$, $\infty P\bar{\infty}$, $P\bar{\infty}$, $2P\bar{\infty}$, $P\bar{\infty}$, ∞P , $\infty P\bar{2}$, $\frac{1}{2}P$, P . The crystals (which attain a height of 3 cm. and a breadth of $2\frac{1}{2}$ cm.) are characterised by a cubical “habit” caused by the predominance of ∞P . In consequence of this development of the prism the pyramidal faces are also enlarged. ∞P is always vertically striated and its foremost edges are deeply indented by the repetition of $P\bar{\infty}$; the other vertical faces are highly lustrous.

Bourmonite from Příbram.—The crystals from this locality are remarkable for the unusual number of faces observed upon them. Their “habit” is tabular through $0P$, and they occur mostly as twins after the law, “the twin plane a face of ∞P .” The following forms were observed:— $0P$, $\frac{1}{2}P$, $P\bar{\infty}$, $P\bar{\infty}$, $\infty P\bar{\infty}$, $\infty P\bar{\infty}$, predominating, P , $\frac{1}{2}P$, $2P$, $\frac{1}{2}P\bar{2}$, $\frac{1}{2}P\bar{2}$, $\frac{2}{3}P\bar{2}$, $P\bar{2}$, $2P\bar{2}$, $\frac{1}{2}P\bar{3}$, $2P\bar{2}$, $\frac{2}{3}P\bar{3}$, $\frac{1}{2}P\bar{\infty}$, $\frac{1}{2}P\bar{\infty}$, $2P\bar{\infty}$, $3P\bar{\infty}$, $\frac{1}{2}P\bar{\infty}$, $3P\bar{\infty}$, $\infty P\bar{\frac{2}{3}}$, $\infty P\bar{2}$, $\infty P\bar{\frac{1}{2}}$, $\infty P\bar{2}$, $\infty P\bar{3}$, secondary; of these $\frac{1}{2}P\bar{\frac{2}{3}}$ and $\frac{1}{2}P\bar{3}$ are new. C. A. B.

Red Vanadinite from the Lead Works on the Ober, near Kappel. By V. v. ZEPHAROVICH (*Jahrb. f. Min.*, 1876, 561—562).—This variety is found together with brown vanadinite prisms, occurring in extremely fine aurora-red needles either singly, more commonly parallel to each other, or in diverging sheaves; their colour is similar to that of crocoite and is new to vanadinite. Some of the crystal-sheaves appear to be brown at one end and red at the other. A microscopical examination showed them to exhibit the usual vanadinite combinations, and a chemical examination resulted in the detection of all the constituents of ordinary vanadinite. The author considers the red colour to be owing to the thinness of the individuals. C. A. B.

Sulphur from Cianciana and Lercara, in Sicily. By V. v. ZEPHAROVICH (*Jahrb. f. Min.*, 1876, 56).—Crystals from Cianciana

are distinguished by their sphenoidal habit, the usual combination being $\frac{+P}{2}$, OP, $P \propto \frac{-P}{2}, \frac{\pm \frac{1}{2}P}{2}$. They are generally pellucid and lustrous. These crystals differ from those of Roccamuto described by G. vom Rath (*Jahrb. f. Min.*, 1873, 591) by the predominance of the half of the pyramid $\frac{1}{2}P$. A fine twin crystal 18 mm. in height and 14 mm. in breadth was observed, the twin-plane and contact-plane being a face of $P\infty$.
C. A. B.

The Mineralogical Composition of the Melaphyr and Augitic porphyry of South Tyrol. By C. DOBLTER (*Jahrb. f. Min.*, 1876, 563—564).—The melaphyr of South Tyrol is divided into hornblende and augitic melaphyr as follows:—(1) *Augite-melaphyr*, (a) augite-porphyr, containing much augite; (b) augite-porphyr, containing less augite, and augite-hornblende-melaphyr. (2) *Hornblende-melaphyr*. (3) Melaphyr, free from augite and hornblende.

The microscopical characteristics are briefly as follows:—*Plagioclase* is the principal constituent, it is mostly clouded and contains numerous enclosures, particularly of glass, ground-mass, magnetite, augite, and apatite; it is also sometimes slightly changed into epidote. *Orthoclase* occurs often, but does not predominate; it closely resembles the plagioclase, and some individuals contain parallel layers of triclinic lamellæ. *Augite* occurs in wine-yellow or colourless crystals and grains, containing enclosures of glass and "ground mass," also magnetite and apatite; it is also occasionally altered into a substance resembling green-earth or into epidote. *Uralite* is also present. *Hornblende* is a common constituent. The magnetite always contains titanium. *Olivine* also occurs in rather large grains, but never microscopical. The "ground mass" consists of felspar with magnetite, occasionally augite and hornblende, and a brown-coloured glass. Secondary formations, such as calcite, epidote, clefsite, chalcedony, and pseudomorphs after hornblende, augite, and olivine, are sometimes observed.
C. A. B.

Organic Chemistry.

Action of Chlorochromic Acid on Organic Bodies. By A. ETARD (*Compt. rend.*, lxxxiv, 127—129).—*Toluene*.—The reaction was moderated by employing an excess of toluene, and by refrigeration. The products were chromium chloride, and an oil boiling at 180°, which was found to consist of a mixture of essence of bitter almonds and chloride of benzyl. It is noteworthy that this reaction between liquids in the cold gave the same product as free chlorine in the gaseous state acting on vapour of toluene at 111°.

Hexane.—This substance was treated similarly to the toluene. Among the products was a small quantity of some acid of the fatty series. The chief result was an oil of aromatic odour, lighter than water, boiling at 150°, oxidisable by chromic acid, and feebly reducing

ammoniacal silver nitrate. Its analysis leads to the formula $C_6H_{11}OCl$, and it is probably a ketone.

Crystallisable Acetic Acid.—A green salt of chromium was the product in this reaction. It contained that metal in the state both of acid and of base, and its composition corresponded with the formula of an hydrated aceto-chromate of chrominum, $Cr_2O_7 \cdot 2[Cr_2(C_2H_3O_2)_5] \cdot 8H_2O$.
R. R.

On the Mercaptides and certain Sulphides of Ethyl. By P. CLAEISSON (*Bull. Soc. Chim.* [2], xxv, 183—187).—A crystalline hydrate of mercaptan, $C_2H_5SH + 24H_2O$, has been observed in the preparation of mercaptan, the author's analyses of this body lead to the formula $C_2H_5SH \cdot 18H_2O$.

Sodium mercaptide may be prepared either by dissolving sodium in mercaptan, or by the action of sodium ethylate on mercaptan. It is a white, very deliquescent mass, which is not crystalline. If sodium mercaptide be heated for two days to $100-120^\circ$ in a current of dry air free from carbonic acid, a substance is obtained soluble in water, which gives a precipitate of sulphite and hyposulphite of barium on addition of nitrate of barium. On evaporating the solution *in vacuo* a white deliquescent sodium salt, $C_2H_5SO_3Na$, is obtained. The author suggests for this salt the constitution $SO_2 \overset{ONa}{\underset{OC_2H_5}{|}}$.

Phosphorus mercaptide, $P(C_2H_5S)_3$, is formed when mercaptan and phosphorus trichloride are heated in sealed tubes to 100° . It is a heavy oil with a disagreeable smell, which decomposes on heating into phosphorus and bisulphide of ethyl.

Arsenic mercaptide, $As(C_2H_5S)_3$, is formed by the action of arsenic trichloride on mercaptan. It is a heavy oil, which boils with decomposition at 150° . A solution of arsenic trichloride in ether reacts with sodium mercaptide to form a heavy oil having the formula $As(C_2H_5S)_3$, which decomposes on heating into arsenic and bisulphide of ethyl.

Antimony mercaptide.—Antimony trichloride combines directly with mercaptan, forming an oil having the composition $SbCl_3 + C_2H_5S$. This oil decomposes on heating to 140° , forming antimony, mercaptan, and hydrochloric acid.

Bismuth mercaptide, $(C_2H_5S)_3Bi$, is formed by adding mercaptan to a solution of nitrate of bismuth. It crystallises in yellow needles, easily soluble in alcohol, less so in ether, which decompose at 200° .

Stannous Mercaptide.—On adding mercaptan to a solution of stannous acetate, a yellow precipitate is formed which is at once oxidised on exposure to air.

Stannic Mercaptide, $Sn(C_2H_5S)_4$, is formed by the action of stannic chloride on mercaptan, both dissolved in bisulphide of carbon. It is a clear oil, which can be distilled *in vacuo* at 200° .

Cadmium Mercaptide, $Cd(C_2H_5S)_2$, is a white amorphous precipitate, insoluble in water, formed by adding mercaptan to acetate of cadmium.

Ethyl tetrasulphide, $(C_2H_5)_2S_4$, is a yellow heavy oil with a disagreeable odour, which cannot be distilled without decomposition into sulphur and bisulphide of ethyl. It is formed by the action of chloride of sulphur on mercaptan dissolved in bisulphide of carbon.

Ethyl pentasulphide, $(C_2H_5)_2S_5$, is produced by heating the tetrasulphide with sulphur in sealed tubes to 140° . It has not been obtained in a state of purity. W. H. P.

Myricyl Alcohol and some of its Derivatives. By L. VON PIEVERLING (*Liebig's Annalen*, clxxxiii, 344—359).—The alcohol was prepared from Carnauba wax by one of the two following processes. The wax is saponified by boiling with alcoholic potash, the alcohol distilled off after filtration, and the soap boiled with a solution of lead acetate. The yellow masses which separate out are washed, dried, and boiled with absolute ether. The wax alcohol crystallises out from the filtered solution in white glittering crystals, and is purified by repeated recrystallisation. In the second method the soapy mass is boiled with dilute hydrochloric acid, and the waxy masses which separate are washed and dried. They are then dissolved in boiling alcohol, the fatty acids removed by ammonia and barium chloride, and the residue, after distilling off the alcohol, is boiled with water and then dried. The myricylic alcohol is then extracted with boiling absolute ether, and purified by repeated recrystallisation. Both these methods yield about 11 per cent.

Myricyl alcohol crystallises from ether in small glittering white needles, which are scarcely soluble in cold alcohol, ether, or benzene, little soluble in cold chloroform, but easily soluble in these media when hot. At 85° it melts to a colourless oil, solidifying at 84° to a white wax. On analysis it gave numbers closely according with those for the formula $C_{30}H_{61}HO$, and not in accord with Maskelyne's formula $C_{31}H_{63}HO$.

Myricyl Iodide.—The alcohol was heated to 120° , phosphorus and iodine were added little by little, and at the end of the reaction the product was dissolved in alcohol and crystallised from ligroin.* It forms small white glistening plates without odour or taste, and scarcely soluble in cold alcohol, ether, or benzene, but easily soluble when they are hot. At 69.5° it melts to a clear colourless oil. On analyses it gave numbers agreeing with the formula $C_{30}H_{61}I$.

Myricyl Chloride.—Prepared by acting with phosphorus pentachloride on myricyl alcohol, and heating the product first in a water-bath, and then in a current of hydrochloric acid. It is purified by repeated solution in hot ether. Myricyl chloride forms a pale yellow, waxy mass, melting at 64.5° , and without odour or taste. It is soluble in alcohol, ether, benzene, and ligroin, but does not crystallise from any of these media. On analysis it gave numbers closely according with the formula $C_{30}H_{61}Cl$.

Myricyl Hydrosulphide.—Formed by the action of an alcoholic solution of myric chloride on potassium sulphide. It is an amorphous yellow powder, without odour or taste, slightly soluble in boiling ether, ligroin and alcohol, easily soluble in boiling benzene and chloroform, forming yellow solutions. It melts at 94.5° to a yellow oil, which solidifies at 93° to a yellow amorphous mass. On analyses it gave numbers agreeing tolerably with the formula $C_{30}H_{61}HS$.

* *Ligroin* is the name given in Germany to the light petroleum oil, b.p. $60-80^\circ$, sp. gr. $0.68-0.70$, sometimes called *benzin*.

Myricylamine.—Prepared by passing a stream of dry ammonia into melted myricyl iodide for more than 24 hours, boiling the whole pulverent mass with alcohol, and crystallising the residue from benzene. It is a yellow, crystalline, heavy body, melting at 78° , nearly insoluble in boiling alcohol and ether, but readily soluble in boiling benzene, toluene, and chloroform. This body appears to be a mixture of the three bases, mono-, di-, and tri-myricylamine, which cannot be separated from another.

Melissic Acid, $C_{30}H_{50}O_2$.—The alcohol was heated with a mixture of potassium hydrate and lime to 220° ; the fused mass was decomposed by dilute hydrochloric acid, and the crude acid washed with warm water. It was dissolved in alcohol, converted into the lead salt, and the lead salt decomposed by an alcoholic solution of hydrochloric acid. Melissic acid crystallises from alcohol in fine glittering scales, consisting of microscopic needles, melting at 88.5° . It is slightly soluble in ether, easily in boiling alcohol, the solutions having a faint acid reaction.

Lead melissate, $Pb(C_{30}H_{50}O_2)_2$, is precipitated by adding an alcoholic solution of potassium melissate to a lead acetate solution. It forms a yellowish powder insoluble in alcohol and ether, soluble in boiling chloroform and toluene, and crystallising from the last in glistening needles.

Silver melissate, $AgC_{30}H_{50}O_2$, is prepared in a similar manner, and forms a white amorphous precipitate, melting at $94-95^{\circ}$, and insoluble in alcohol and ether, but soluble in boiling chloroform.

Copper melissate, $Cu(C_{30}H_{50}O_2)_2$, forms a bright green precipitate, soluble in chloroform.

Potassium melissate, $KC_{30}H_{50}O_2$, is formed by adding a boiling alcoholic solution of the acid to a concentrated aqueous solution of potassium carbonate. It crystallises from alcohol in white glittering needles, which are soluble in twenty parts of water.

Ethyl melissate, $C_2H_5.C_{30}H_{50}O_2$, is prepared by the action of ethyl iodide on silver melissate, and forms a white waxy body easily soluble in alcohol and ether. It fuses at 73° to a clear oil, which solidifies at 72° to a white wax, inodourless and tasteless. By boiling potassium hydrate solution, it is decomposed into potassium melissate and alcohol.

Amyl melissate, $C_5H_{11}.C_{30}H_{50}O_2$, was obtained by dissolving melissic acid in amyl alcohol (132° b. p.), and saturating with gaseous hydrochloric acid. White waxy needles, without odour or taste, and soluble in alcohol, ether, benzene, and chloroform. It melts at 69° , and solidifies at 67° to a mass resembling paraffin.

Myricyl cyanide $C_{30}H_{48}CN$, was prepared by acting with myricyl iodide on potassium cyanide, washing with alcohol, and dissolving in benzene. On evaporation of the benzene it remains behind as a white amorphous body, melting at 75° to a yellow oil, and soluble in hot benzene, though scarcely soluble in alcohol, ether, or chloroform.

From the mother-liquors from the preparation of myricyl alcohol was separated a small quantity of a waxy alcohol, melting at 80° . On

analysis it gave numbers agreeing with the formula $C_{27}H_{55}O$, whence it is probably ceryl alcohol. E. N.

On some Derivatives of Dialdol. By AD. WURTZ (*Compt. rend.*, lxxxiii, 1259).—During the preparation of aldol, especially if the contact of the hydrochloric acid with the aldehyde is prolonged, the liquid acquires a dark brown colour. If this brown liquid is diluted with water and neutralised with sodium carbonate, a black oil separates, which, on standing, deposits crystals. After this oil has separated, a semi-solid, yellowish-brown substance is deposited. It is collected on a filter, strongly pressed between blotting paper to separate adherent oily substances, and boiled with water, whereupon it melts into large oily drops which slowly dissolve. The aqueous solution deposits crystals on cooling, but the whole quantity of substance is not deposited for some days, as the solution remains supersaturated for a long time. The crystals are purified by repeated crystallisation from water, and are identical with the substance which is deposited from crude aldol. The body is formed by the abstraction of one molecule of water from two molecules of aldol, and is therefore named dialdane,—



It is slightly soluble in cold water, more so in hot water. The boiling saturated solution deposits small plates or crystalline grains, and the solution remains supersaturated for a long time. After standing for a fortnight the cold solution contained 4 p. c. of dialdane; if, however, a solution be made in the cold, it contains only 0.692 per cent.

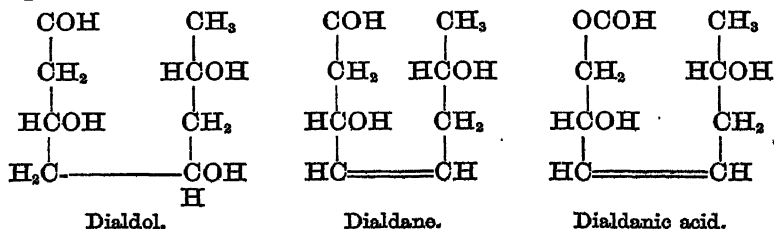
Dialdane is very soluble in hot alcohol, much less so in ether. It melts at $139-140^\circ$, and remains in a state of superfusion for a long time. It can be distilled in a vacuum, and the distillate is colourless and viscid, solidifying after some time to a crystalline mass. In contact with sodium amalgam in acid solution it takes up hydrogen, and when evaporated to dryness in a water-bath, and treated with alcohol, it yields a viscid, colourless substance, having a slightly bitter taste, distilling at $185-195^\circ$ under a pressure of 3 cm.

Dialdane reduces silver salts very quickly. Heated with oxide of silver it forms an acid and evolves acrid vapours. The potassium salt of the same acid is formed by treating dialdane with potassium permanganate.

This acid is derived from dialdane by addition of one atom of oxygen, and is called *dialdanic acid*, $C_8H_{14}O_2 + O = C_8H_{14}O_4$. It is isomeric with suberic acid, but is monobasic and does not resemble that body in any of its properties. It may be obtained from its potassium salt by means of sulphuric acid, and subsequent treatment with ether, and is left as a crystalline mass on evaporation of the ether. The silver salt is soluble in water and furnishes the acid by treatment with hydrogen sulphide. After purification the acid is obtained by crystallisation from water in the form of large, brilliant, colourless crystals, derived from a clinorhombic prism; they melt at 80° ; can be distilled in a vacuum at a temperature of 198° ; are very soluble in alcohol and water, less so in ether. The aqueous solution is strongly acid, and neutralises bases completely.

Potassium dialdante, $C_8H_{13}KO_4$, is formed by saturating the acid with potassium carbonate. It is soluble in water and alcohol, and is deposited from the hot solutions in transparent crystals, becoming opaque and deliquescent when exposed to the air. The *sodium salt* is soluble in water and alcohol, and crystallises in transparent plates. The *barium salt* is uncrystallisable, drying up to a hard, glassy mass, soluble in alcohol, and precipitated by ether in a pulverulent form. *Calcium dialdante*, $(C_8H_{13}O_4)_2Ca$, is very soluble in water, and is obtained by evaporation of the aqueous solution in crystals which contain water and are not deliquescent. The zinc, lead, and silver salts are also very soluble in water.

The properties of dialdane prove it to be an aldehyde, and, since dialdanic acid is monobasic, it can contain only one carboxyl group, CO_2H , and consequently the aldehyde itself can contain only one group, COH . Dialdane is formed, therefore, from two molecules of aldol, by the action of CO_2H in one molecule on CH_3 in the other, and subsequent elimination of water:—



C. W. W.

Optical Properties of Mannite. By A. MÜNTZ and E. AUBIN (*Compt. rend.*, lxxxiv, 126).—The authors claim, in their study of the general problem of the relations between the optical properties of mannite, and those of the sugar from which the mannite is derived, to have been the first to examine the properties of mannites derived from levogyrotary sugars.

R. R.

Purification of Valeric Acid. By LESCOEUR (*Bull. Soc. Chim.* [2], xxvii, 104).—Valeric acid may be prepared in a great state of purity from the valerates of potassium and sodium. One equivalent of neutral valerate is dissolved in a little more than two equivalents of valeric acid by heating, and the solution left to crystallise in a cool place. The crystals are dried on a porous tile and afterwards submitted to pressure between several folds of filter-paper. By treatment with tepid water the acid salt can be decomposed and valeric acid liberated, but a better method consists in submitting the product to distillation; below 200° only water passes over, and when the temperature reaches 300° the distillation must be stopped. The first portion of the distillate being rejected the remainder is pure valeric acid. It boils at 174° at 770 mm. pressure, remains liquid at 15° , has a density of 0.948 at 14.5° , and produces right-handed rotation upon a ray of polarised light.

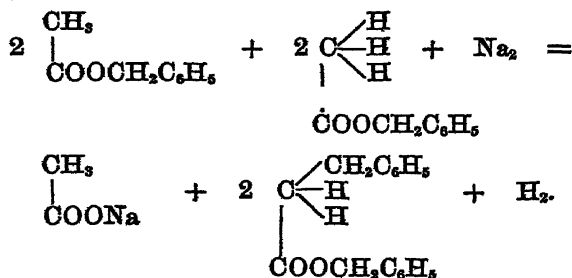
H. H. B. S.

Normal Valeric Acid from Normal Caproic Acid. By E. ERLÉNMEYER (*Deut. Chem. Ges. Ber.*, ix, 1840).—Bromocaproic acid is made alkaline with carbonate of soda, and decomposed with sulphuric acid, and the oxycaproic acid is extracted with ether, and oxidised after expulsion of the ether, with chromic acid mixture. A volatile acid appears in the distillate possessing all the properties of normal valeric acid.
C. L. F.

Nitro-stearic Acid. By P. CHAMPION and H. PELLET (*Chem. Centr.*, 1876, 37).—This acid, $C_{36}H_{36}(NO)_4O_4$, is a light yellow powder, prepared by the action of a large excess of a cooled mixture of sulphuric and nitric acids upon powdered stearic acid. The product of this action is mixed with water, the solid is collected, washed with water, and purified by digestion with alcohol.
M. M. P. M.

New Method of Synthesis of Aromatised Fatty Acids. By M. CONRAD and W. R. HODGKINSON (*Deut. Chem. Ges. Ber.*, x, 254—256).—When benzyl acetate (300 grams) is heated to 120° with sodium (12 grams), a violent reaction takes place, attended with evolution of hydrogen. The chief products of the reaction are sodium acetate and an oily body, boiling above 300° , and giving on analysis numbers agreeing with the formula $C_{16}H_{16}O_2$. The latter product, when boiled with baryta-water, is decomposed and yields a barium salt, the acid of which agrees in composition with the formula $C_8H_{10}O_2$, melts at 46° , and has the characteristic properties of β -phenylpropionic or hydrocinnamic acid. From these facts the authors conclude that the substance $C_{16}H_{16}O_2$ is the benzyl-ether of the acid just named, or *hydrocinnamēin*.

It appears, therefore, that benzyl acetate is not acted on by sodium in the same manner as the acetic ethers of the fatty series, but that the reaction takes place mainly in accordance with the following equation:—



Benzyl butyrate similarly treated yields the benzyl-ether of phenylvalerianic acid,—a liquid boiling at 240 — 250° under a pressure of 120 mm. This substance is decomposed by boiling baryta-water, yielding an acid melting at 78° , which is being further examined.

J. R.

The Acids $C_8H_8O_4$. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, ix, 1821—1823).—By the action of zinc-dust and alcohol on the three

acids, $C_5H_6O_4$, the author obtained a pyrotartaric acid which seemed at first, from the solubility of its lead-salt, to differ from that which Kekulé and Markownikoff obtained by the action of sodium amalgam on the same acids. But experiments on the calcium salts proved them to be identical. The author observed that there was a decided difference in the violence and speed of the reaction with the three isomeric acids, the citraconic acid being more speedily and completely acted on than itaconic, and mesaconic more rapidly than either, but the action is not so complete.

Citraconic acid is also produced in the formation of pyrotartaric from pyrrocemic acid, which explains the formation of mesaconic acid when pyrrocemic acid is acted on by concentrated hydrochloric acid, citraconic acid being first formed and then converted into mesaconic acid. From the above facts the author is led to propose for citraconic acid the formula—



Citric Acid. By E. FLEISCHER (*Arch. Pharm.*, [3], ix, 320—343).—The author's results—in which there is nothing particularly new—are chiefly these:—

1. The crystals of citric acid which form from saturated solutions have the formula $C_{12}H_6O_{12} \cdot 4HO$.*

2. The anhydrous acid has the composition $C_{12}H_6O_{12}$ or $C_4H_2O_4$: the usual formula, $C_{12}H_8O_{11}$, is regarded by the author as incorrect.

3. Citrates are decomposed at varying temperatures, with production of aconitic acid.

4. The neutral citrates of barium, calcium, and lead are represented by the general formulæ $MO \cdot C_4H_2O_4$ or $3MO \cdot C_{12}H_6O_{12}$.

5. The basicity of citric acid is not decided by the author's experiments: he thinks that it may be most simply regarded as monobasic.

The results are for the most part based on analyses of only a few salts. M. M. P. M.

Simple Method of preparing Metallic Cyanides. By E. ERLÉNMEYER (*Deut. Chem. Ges. Ber.*, ix, 1840).—By the fusion of dehydrated ferrocyanide of potassium with sodium, a white substance is obtained containing 40 per cent. of cyanogen in the form of cyanide of the alkali-metal, nearly all of which can be poured off from the separated molten iron. C. L. F.

Dehydrotriacetoneamine. By W. HEINTZ (*Liebig's Annalen*, clxxxiii, 276—282).—This base was found, together with triacetoneamine, in the mother-liquor of diacetoneamine oxalate. It forms a platinumchloride, which is but sparingly soluble in water; the free base, which is an oily liquid, and its salts, oxidise rapidly in the air. C. S.

* C = 6; O = 8.

A Sixth Acetone-base. By W. HEINTZ (*Liebig's Annalen*, clxxxiii, 283—289).—The mother-liquor of diacetoneamine oxalate also contains a base, which appears to be dehydrodiacetoneamine, $C_6H_{11}N$. C. S.

Alcohol-bases formed by the Hydrogenisation of Di- and Triacetoneamine. By W. HEINTZ (*Liebig's Annalen*, clxxxiii, 290—316).—By acting with sodium amalgam on a solution of diacetoneamine hydrochloride in a mixture of aqueous ammonia and alcohol, *diacetonealkamine*, $C_6H_{15}ON$, is produced. The free base is a liquid which is soluble in water, has a slight ammoniacal smell, and an aromatic alkaline taste; it boils at $174-175^\circ$. Its hydrochloride forms a syrupy liquid, and the platinochloride, which is readily soluble in hot water, forms orange-coloured triclinic crystals $(C_6H_{15}ON, HCl)_2PtCl_4$. The normal oxalate forms microscopic prisms, and the acid salt crystallises in small plates. When carbon dioxide is passed into a solution of the base in ether, a white precipitate is obtained, crystallising from water in small plates or needles, which seem to be an acid carbonate.

When a solution of triacetoneamine in dilute alcohol is treated with sodium amalgam, it is converted into *triacetonealkamine*, $C_9H_{19}ON$, and the isomeric *pseudotriacetonealkamine*. The latter is but sparingly soluble in water and ether, and crystallises from a hot alcoholic solution on cooling. It melts at about 180° , and slowly sublimes. The platinum salt forms rhombic crystals $(C_9H_{19}ON, HCl)_2PtCl_4 + 5H_2O$.

Triacetonealkamine crystallises from hot water in probably quadratic octohedrons, and has a slightly sweet and burning taste. It melts at 128.5° , but begins to sublime at 100° . The hydrochloride crystallises from hot water in needles or plates. Its platinum double salt is freely soluble in water, sparingly in alcohol, and not in ether, and is anhydrous. C. S.

A New Platinum Salt containing two Ammonium Bases. By W. HEINTZ (*Liebig's Annalen*, clxxxiii, 317—320).—This salt, which was obtained accidentally in preparing the preceding compound, is formed when equivalent quantities of the platinochlorides of triacetoneamine and triacetonealkamine are dissolved in water, and forms quadratic plates. C. S.

Researches on Essence of Turpentine. By G. PAPASOGLI (*Gazzetta chimica italiana*, vi, 538—542).—The author finds that essence of turpentine has not the property of converting oxygen into ozone as generally supposed, but on the contrary ozone is decomposed by contact with it. It possesses, however, the property of absorbing both oxygen and nitrogen almost equally.

Sodium, when placed in essence of turpentine in contact with the air, gradually disappears, and is replaced by a transparent substance of a dark maroon colour insoluble in the turpentine, the excess of the latter remaining unchanged. The dark-coloured substance, after the particles of unattacked sodium had been removed, was freed from turpentine as far as possible by pressure, and dissolved in water. On carefully neutralising this solution with nitric acid, and adding lead

acetate, a precipitate was obtained, which, after being washed with alcohol, was suspended in water and decomposed by hydrogen sulphide. The precipitate was then exhausted with boiling water, and the solution evaporated, when it yielded a small quantity of an acid crystallising in long needles of a dark red colour. This is only slightly soluble in cold water, but very soluble in alcohol and ether. It melts at 97° . The quantity obtained was too small to permit of analysis, and it was found that the salts formed with the alkali-metals were not crystalline and very soluble in water.

The ordinary liquid tetrabromo-terebenthene, $C_{10}H_{12}Br_4$, was dissolved in ether and submitted to the action of metallic sodium; saline crusts were formed on the surface of the metal which, when removed and washed with ether, were found to consist of sodium bromide and a body of resinous aspect, insoluble in water, alcohol, ether, and benzene, but very soluble in chloroform. As on analysis, it was found to contain about 70 per cent. bromine, the author considers it to be a solid modification of the tetrabromo-derivative, $C_{10}H_{12}Br_4$. The ethereal solution, on further treatment with sodium, yielded a bright yellow brominated compound insoluble in all ordinary solvents.

Terebenthene hydrochloride.—It is known that when hydrochloric acid is passed into essence of turpentine, two different modifications of the compound, $C_{10}H_{16}HCl$, are obtained according to the temperature at which the operation takes place, the solid modification being formed at 0° , and the liquid at 100° . The author finds that if the essence is quite pure, the solid modification may be obtained at 15° , but if it contains the smallest quantity of altered turpentine the liquid gradually acquires a brown tint, and ultimately becomes quite black if much impurity is present. This reaction may be taken advantage of to ascertain the purity of the turpentine. The first product of the action of chlorine on the hydrochloride is *monochloroterebene hydrochloride*, $C_{10}H_{14}Cl.HCl$. It melts at 107° , and may be crystallised from alcohol. The corresponding bromine-derivative melts at 80° . C. E. G.

Cumol. By E. PATERNO and P. SPICA (*Gazzetta chimica italiana*, vi, 535—537).—The cumol was prepared from the cumene (isopropylbenzene) from cumic acid, by converting it into potassium cumene-sulphonate, and fusing it with potassium hydrate in the usual manner. The crude oily product which separates on acidifying the solution of the fused mass, was separated from the water which it obstinately retains, and purified by fractional distillation. Cumol, $C_6H_4(C_3H_7).OH$, crystallises in colourless needles, which melt at 61° . It boils at $228.2-229.2^{\circ}$ (cor.) at a pressure of 758.18 (cor. to 0°). The methyl derivative, $C_6H_4(C_3H_7).OCH_3$, was prepared by heating a solution of equal molecular weights of cumol and potassium hydrate in methyl alcohol, with a slight excess of methyl iodide. It is a colourless highly refractive liquid, which possesses an odour recalling that of aniseed. Its specific gravity at 0° is 0.962, and it boils at $212-213^{\circ}$ (cor.) under a pressure of 758.04. The acetyl derivative, $C_6H_4(C_3H_7).OC_2H_3O$, was obtained by acting on cumol with excess of acetyl chloride. Its specific gravity at 0° is 1.026, and it boils at $244-244.5^{\circ}$ (cor.) under a pressure of 756.27.

In order to ascertain the constitution of the cumol prepared in the manner above described, its methyl-derivative was submitted to oxidation by a mixture of potassium bichromate and sulphuric acid. A small quantity of an acid was obtained which from its fusing point appeared to be anisic acid. If this is confirmed, the cumol must be a para-derivative of benzene. The authors intend continuing their researches on this substance, and also on the corresponding cumol from propylbenzene; which hydrocarbon appears to yield two isomeric sulphonic acids.

C. E. G.

Crystallo-optical Investigation of certain Camphor Derivatives. By V. ZEPHAROVICH (*Chem. Centr.*, 1876, 260).—1. Camphoric acid, $C_{10}H_{16}O_4$. 2. Oxycamphoric acid, $C_9H_{12}O_6$. 3. Indifferent compound, $C_9H_{12}O_2$. 4. Hydroxycamphoronic acid, $C_9H_{14}O_6$. 5. Pimelic acid, $C_7H_{12}O_4$. 6. Acid lead sulphocamphorate, $C_{13}H_{20}PbS_2O_{12} \cdot 4H_2O$.

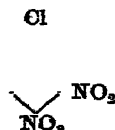
Nos. 1 to 3 form monoclinic, Nos. 4 and 5 triclinic crystals. No. 2 is dimorphous, being monoclinic in both forms; the former differ in optical properties, and in cleavage.

M. M. P. M.

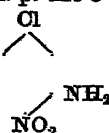
Orthodinitro-compounds. By AUG. LAUBENHEIMER (*Deut. Chem. Ges. Ber.*, ix, 1826, 1827).—The action of ammonia on dinitro-chlorobenzene (that obtained by the nitration of metachloronitrobenzene) yields nitrite of ammonia and chloronitraniline, which, when purified, crystallises in long thin yellow plates, melting at 123.5° . On decomposition with ethyl nitrite, it yielded a paranitrochlorobenzene, melting at 83° , which on reduction with zinc and hydrochloric acid, gives chloraniline melting at 69.5° .

This would give to the following bodies the subjoined constitutions:—

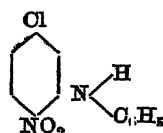
Nitro-m-chloronitrobenzene.



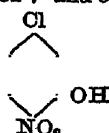
Chloronitraniline.
m. p. 123.5° .



Chloronitrodi-phenylamine.



Chloronitrophenol.
m. p. 32.7° and 38.9° .



This chloronitraniline is identical with that prepared by W. Koerner, and by Beilstein and Kurbatow from paranitrometadichlorobenzene.

From the reactions of ammonia on nitro-m-bromonitrobenzene, and nitro-m-chloronitrobenzene (in which the nitro-groups stand in the orthoposition to one another), the author infers that this position is necessary for the reaction, especially as in the meta- and para-halogen compound, such reactions had not been noticed.

When orthodinitrobenzene is heated with dilute caustic soda, it dissolves, with evolution of ammonia, forming sodium nitrate, and the sodium-derivative of orthodinitrophenol. The nitrophenol (prepared from the scarlet barium-salt) was yellow, and melted at 44.8° , and volatilised in a current of steam.

The above facts point to the conclusion that all orthodinitro-com-

pounds yield, on heating with caustic soda, a phenol and nitrite of sodium, and when treated with alcohol and ammonia, an amido-compound and nitrite of ammonia. C. L. F.

Benzenesulphonic Acid and its Derivatives. By H. LIMPRICHT (*Deut. Chem. Ges. Ber.*, ix, 1858—1868).—The author is at present engaged in a study of the bromobenzenesulphonic acids, and has followed Nolting's process, viz., treating with bromine the silver salts of benzenesulphonic, ortho-, meta-, and parabromobenzenesulphonic, metanitrobenzenesulphonic, and ortho-, meta-, and paramidobenzenesulphonic acids. The silver salts were made by neutralising the respective acids with silver carbonate, and shaking the filtered solutions with bromine as long as a precipitate of silver bromide was formed.

Metabromobenzenesulphonic Acid.—The silver salt of the acid prepared by the process already described was converted into the barium salt, which was recrystallised, converted into the chloride and then into the amide, and in no case was there a trace of ortho- or para-acid formed. The silver salt of this acid, again treated with bromine, gave three acids, which were separated by fractional crystallisation of their barium salts; (1.) *Barium metadibromobenzenesulphonate*, which is the most abundant, crystallises in the well known hard needles: (2.) The

barium salt of *paradibromobenzenesulphonic acid*, $\text{Br} \begin{array}{c} \text{SO}_3\text{H} \\ | \\ \text{C}_6\text{H}_3\text{Br}_2 \end{array}$, crystal-

lises in long, concentrically-grouped needles. The corresponding *chloride* melts at 71° ; the *amide* at 193° . The salts resemble those of the *meta*-acid. (3.) The barium salt of *orthodibromobenzenesulphonic acid*, SO_3H

$\begin{array}{c} \text{C}_6\text{H}_3\text{Br}_2 \\ | \\ \text{Br} \end{array}$, is found in small quantity only, and is very difficult to

separate from the other two. The corresponding acid, whose amide melts at 167° , is identical with the acid which Goslich obtained by acting on parabromobenzenesulphonic acid with bromine, so that it must have the constitution just given.

Orthodibromobenzenesulphonic acid was prepared by treating parabromobenzenesulphonic acid with bromine. It crystallises in needles with three molecules of water, and melts at 57 — 58° . The potassium, ammonium, and silver salts crystallise in needles, and are anhydrous. The calcium salt is also anhydrous, and crystallises in plates. The barium and lead salts are difficult to dissolve, and crystallise with $2\text{H}_2\text{O}$. The chloride melts at 31° and the amide at 170° . The acid was boiled with

nitric acid, and gave *nitrodibromobenzenesulphonic acid*, $\text{C}_6\text{H}_2 \begin{cases} \text{NO}_2 \\ \text{Br}_2 \\ \text{SO}_3\text{H} \end{cases}$.

The potassium and ammonium salts are anhydrous and yellow; the barium and lead salts contain $3\text{H}_2\text{O}$, and the calcium salt 4, or $6\text{H}_2\text{O}$. The chloride melts at 98 — 99° , and the amide at 210 — 211° .


Tribromobenzenesulphonic acid was prepared from the silver salt of

the dibrominated acid just described. The barium salt crystallises with 3 and with 5 molecules of water; the chloride melts at 120—121° and the amide at 152°.

Orthobromobenzene sulphonate of silver, when treated with bromine gave a mixture of two *dibromobenzenesulphonic* acids, which were separated by means of their chlorides. The first, probably the *para*-acid, gave a chloride melting at 71°, and an amide melting at 192°, while the chloride of the second melted at 97—98°, and the amide at 252°.

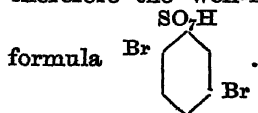
The silver salt of nitrobenzenesulphonic acid, $C_6H_4(NO_2)SO_3H$, remained unchanged when treated with bromine. *Silver paramidobenzenesulphonate*, on similar treatment, yielded only tribromaniline. The *ortho*-salt also gave tribromaniline, but yielded besides an acid which was proved by analysis to be bromobenzenesulphuric acid. The *meta*-acid, when its silver salt is treated with bromine, gives a beautiful violet colour. A precipitate is formed consisting of dibromo-metamidobenzenesulphonic acid, unchanged amidobenzenesulphonic acid, and silver bromide. The blue colouring matter was extracted from the evaporated liquid with alcohol. It is amorphous, and dissolves with an intense violet colour in water and in alcohol, but is insoluble in ether. The colour is destroyed by tin and hydrochloric acid, but reappears on careful addition of bromine. The blue substance is an acid: it decomposes carbonates, forming non-crystalline deep-blue salts. It appears to be a mixture of two dibrominated amidobenzenesulphuric acids, but must also, from its decomposition-product, contain tri- and tetrabromo-acids. The dry acid appears on analysis to have the formula $C_6H_2Br_2(NH_2)SO_3H$. Nitrogen trioxide converted it into the di-azo-compound, which, with alcohol, was decomposed into an acid the barium salt of which was analysed. It had the formula $C_6HBr_4SO_3H$. The bromine by theory is 59 per cent., that found 48·3 per cent. On recrystallisation of the barium salt the percentage of barium rose to that required for a tribromo-acid. The diazo-acid, when decomposed with hydrobromic acid gave a tribromo-acid the barium salt of which had a violet-colour.

The author has prepared a number of the salts of the *nitrometa-bromobenzenesulphonic acid* discovered by Bernthsen, and studied by

Alfred Thomas. Its formula is NO_2 . The potassium and

ammonium salts are yellow and contain no water. The barium and lead salts crystallise in yellow needles with $3H_2O$; the calcium salt is nearly white and contains $6H_2O$. The silver salt crystallises in delicate white needles with $1\frac{1}{2}H_2O$; the chloride melts at 83°, and the amide at 169—170°. The *amido-acid* obtained by reducing the one just described with tin and hydrochloric acid, forms large white concentrically grouped needles; 100 grams of water at 22° dissolve 0·579 gram. The potassium salt crystallises in anhydrous prisms; the barium salt in warts with $1\frac{1}{2}H_2O$, and the lead salt in needles with $2H_2O$. When treated with hydriodic acid the amido-acid is converted into *orthoamidobenzenesulphonic acid*. The amido-, and, consequently,

the nitro-group must occupy either the position 1 or 6. To decide this, the amido-acid was converted into the diazo-compound, which on treatment with hydrobromic acid, gave *dibromobenzenesulphonic acid*. Its potassium and barium salts, and the chloride and amide were prepared. The chloride melted at 70.5, and the amide at 197°. It is therefore the well-known paradibromobenzenesulphonic acid of the



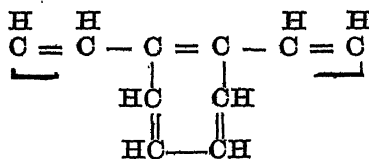
Nitroamidobenzenesulphonic acid, $\text{C}_6\text{H}_3(\text{NH}_2)(\text{NO}_2).\text{SO}_3\text{H}$, was prepared by heating the nitrobromo-acid to 130° with alcoholic ammonia, and crystallises in easily soluble yellow needles. Its barium salt crystallised with $1\frac{1}{2}\text{H}_2\text{O}$.

W. R.

Nitroderivatives of Salicylic Aldehyde. By G. MAZZARA (*Gazzetta chimica italiana*, vi, 460—461).—On boiling salicylic aldehyde with 3 parts of nitric acid diluted with twice its volume of water, an oil is obtained which solidifies to a crystalline mass on cooling. This consists of two isomeric mononitroderivatives which were separated by taking advantage of the difference in solubility of their barium compounds. The less soluble salt crystallises with two molecules of water in beautiful yellowish-red prisms, and the nitroderivative separated from it, in small yellow prisms melting at 105—107°. The more soluble barium compound crystallises in yellow prisms containing at least 6 mols. of water: the corresponding nitro-compound forms needles which melt at 123—125°. Both the barium salts lose their water of crystallisation below 100°. The author also states that when the dichlorocresol produced by the action of phosphorus perchloride on the aldehyde is treated with sodium or potassium ethylate, salicylic aldehyde is regenerated.

C. E. G.

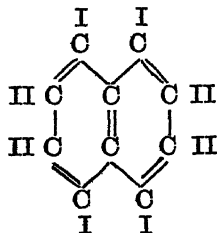
Researches on the Naphthalene Group. By C. LIEBERMANN (*Liebigs Annalen*, clxxxiii, 225—275).—Erlenmeyer in 1866, was the first to express the constitution of naphthalene by what may be termed a benzene-formula, viz.:



Graebe's experiments which followed supported this view. Naphthalene is thus regarded as a double benzene in which two carbon atoms are common to both benzene groups. The combination of this view with those of Kekulé for the benzene derivatives, received most satisfactory support from the results obtained by Merz, with the two isomeric naphthalene-monosulphonic acids with their isomeric transformation products, and more recently still from the experiments of

Aronheim, in the course of which he effected the synthesis of naphthalene from phenylbutylene. The investigations here described were undertaken for the purpose of throwing additional light on the above subject, and to effect, if possible, a solution of the question of the theoretical constitution of naphthalene.

In Erlenmeyer and Graebe's formula, as Merz has shown, there are two ways in which a substituting atom or atomic group may enter naphthalene:



Either one of the four hydrogen-atoms under I, or one of the four under II can be replaced. Thus in the two isomeric naphthalene sulpho-acids distinguished as α and β , the sulphuryl group of the one must occupy the position I, and that of the other the position II. But which of them has the sulphuryl group in the position I or II is not yet definitely known. Up to this time the mono-substitution products of naphthalene have only been separated into two classes, in one of which (α) the substituting group or element takes up the same position as the sulphuryl-group in the so-called α -naphthalene sulpho-acid, whilst the β -substitution-products are represented by the β -sulpho-acid. In compounds not arising from the sulpho-acids, the demonstration of the α or β position is effected by transformations. Thus nitronaphthalene and the naphthylamine obtained from it belong to the α -group, because the latter compound, by means of the diazo-reaction, is convertible into α -naphthol (Griess); and bromonaphthalene is the α -compound, because when treated with sodium and chloro-carbonic ether it passes into the α -naphthoic acid (Elghis). Whilst some α -products are obtainable directly from naphthalene, the hitherto known β -derivatives are conversion-products of the β -sulpho-acid, and are never obtained from naphthalene by direct reactions. The β -derivatives, however, are not numerous. The object of the following investigations was to increase the number of these latter derivatives from other starting points than the sulpho-acid, and further to examine the isomeric disubstitution-products, in order to fix the exact place in naphthalene which has hitherto been termed α . The problem can be solved by taking any naphthalene disubstitution-product in which both substitution-groups (substituents) (1) are contained in the same benzene group; (2) both exist in the α or both in the β position, and the relative position of the two substituents is known.

Supposing the latter to be 1 : 2, then the substitution has taken place on the carbon atoms II; if 1 : 4, the substituents will be on the carbon atoms I. In this case the position 1 : 3 is excluded.

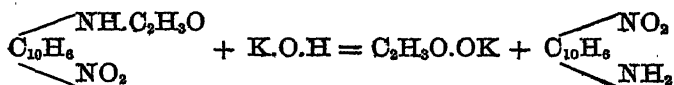
Rother, with the author, brominated acetonephthalide, obtaining bromacetonephthalide, $\begin{array}{c} \text{NH.C}_2\text{H}_5\text{O} \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_6 \\ \diagdown \quad \diagup \\ \text{Br} \end{array}$, and proved that the bromine atom represented an α -hydrogen atom, to which category the atom represented by the acetamide group also belonged.

Experiments to determine the α -Position.—Nitracetonephthalide.
 $\begin{array}{c} \text{NH.C}_2\text{H}_5\text{O} \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_6 \\ \diagdown \quad \diagup \\ \text{NO}_2 \end{array}$. For the preparation of large quantities of aceto-

naphthalide it was found advantageous to treat naphthylamine for a long time with boiling glacial acetic acid. 400 grams of naphthylamine were boiled uninterruptedly for four to five days in retort with inverted condenser with 500 grams of glacial acetic acid. The mass obtained on cooling was rubbed up with water, washed, and recrystallised from boiling water. The melting point of the pure substance is 159° . To obtain nitracetonephthalide, a cold saturated solution of acetonephthalide in glacial acetic acid was mixed with pure fuming nitric acid in the proportion of one part of the nitric acid to three parts of acetonephthalide. The cold mixture was allowed to stand for eighteen hours. The required body is found partly as a crystalline crust at the bottom of the vessel, partly in the acetic-acid solution. Only that found crystallised was taken to avoid impurity; and this was purified by recrystallising from glacial acetic acid. The nitracetonephthalide contained in the acetic mother-liquors, and precipitable therefrom by water, was afterwards used for preparing dinitracetonephthalide.

The nitracetonephthalide crystallised between 170 — 172° , nearly agreeing with the results of Andreoni and Biedermann. On closer examination it was, however, found that this substance was actually a mixture of two isomeric nitracetonephthalides, possessing nearly the same solubility and a common melting point of 171° . These isomerides yield two isomeric nitronaphthols, one of which melts at 164° , the other, obtained in small quantity only, at 128° . An endeavour was made to convert the aceto-compounds into nitronaphthylamine and here to effect a separation. It was, however, only found possible to obtain pure that nitronaphthylamine which is contained in largest quantity and corresponds with the nitronaphthol melting at 164° . The nitronaphthylamine occurring in largest quantity, with its derivatives, is marked α , the other β .

α -Nitronaphthylamine.—Prepared by heating an alcoholic solution of 4 parts by weight of nitracetonephthalide with from 1 to $1\frac{1}{2}$ parts of solid potassium hydrate, to gentle boiling for an hour with inverted condenser:



α -Nitronaphthylamine.—This body crystallises in thin, orange-coloured needles. The melting point is about 191° . It has great tinctorial power for wool, colouring it a fine orange-yellow. It dissolves with great difficulty in water, with less difficulty in alcohol and

acetic acid. Its basic character is nearly lost by the presence of the nitro-group. It dissolves on warming with acids more easily than in pure water, but is reprecipitated unaltered on cooling. Beilstein and Kuhlberg obtained a nitronaphthylamine by partial reduction of the dinitronaphthalene melting at 212° . This is an isomeride, consisting of shining red crystals, melting at 118° to 119° and forming salts.

β -Nitronaphthylamine is contained, together with the α -isomeride, in the mother-liquors left on recrystallising the latter body from alcohol. It could not be got quite pure. It was found to melt at about 158° and to resemble the α -compound closely.

Nitronaphthalene from α -nitronaphthylamine.—Nitrous acid vapours are passed into a well-cooled mixture of α -nitronaphthylamine and some dilute sulphuric acid. The solution is filtered quickly into a large quantity of alcohol, and this is boiled till no more nitrogen is given off. The alcohol is distilled off and replaced by water. The oil obtained solidifies after some days. The mass is recrystallised from alcohol. The body forms long, yellowish needles. It is identical with the ordinary α -nitronaphthalene melting at 58° . By reduction with acetic acid and iron filings it was converted into α -naphthylamine melting at 49.5° . It is therefore proved that the nitro-group in α -nitronaphthalene is in the α -position, and hence the body is thus

constituted, $\text{C}_{10}\text{H}_6 \begin{matrix} \swarrow \text{NO}_2(\alpha) \\ \searrow \text{NH}_2(\alpha) \end{matrix}$. In the production of the chief product of

the nitration of aceto-naphthalide the same hydrogen is replaced by the nitro-group as is replaced by bromine in brominating the same body.

The Diazo-reaction with β -Nitronaphthylamine.—This body was obtained not quite pure and only in small quantity. It was treated with nitrous acid and the product recrystallised from alcohol, when long, thin needles were obtained melting at 199° . By boiling with sodium hydrate solution, ammonia and β -nitronaphthol were obtained. The crystals on analysis did not give very satisfactory results, but these pointed to a probability of their consisting of either a dinitrazo-

oxynaphthalene, $\text{C}_{10}\text{H}_6(\text{NO}_2)-\text{N} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{N}-\text{C}_{10}\text{H}_6(\text{NO}_2)$, or of a double compound of this

with nitronaphthol, $[\text{C}_{10}\text{H}_6(\text{NO}_2)]\text{N}_2\text{O} + \text{C}_{10}\text{H}_6(\text{NO}_2)\text{OH}$. The latter agreed best with results obtained, and, as above-mentioned, β -nitronaphthol was obtained by boiling with soda. Further experiments with larger quantities demonstrated the extreme difficulty of obtaining even very small quantities of the β -nitronaphthalene.

Reduction of Nitracetonaphthalide.—This body was treated with granulated tin and hydrochloric acid, and the product obtained was dissolved, after draining, in boiling water, and sulphuretted hydrogen was passed through the solution. After filtering from the tin sulphide, the filtrate is excluded from the air to prevent decomposition, which would otherwise take place, with violet coloration. On cool-

ing, hydrochloride of amidacetonaphthalide, $\text{C}_{10}\text{H}_6 \begin{matrix} \swarrow \text{NHCOCH}_3 \\ \searrow \text{NH}_2\text{HCl} \end{matrix}$, separates from the solution in long, white needles.

Chromate of Amidoacetonnaphthalide, $\left(\begin{array}{c} \text{NH.C}_2\text{H}_5\text{O} \\ \text{C}_{10}\text{H}_6 \\ \text{NH}_2 \end{array} \right)_2 \text{H}_2\text{Cr}_2\text{O}_7$. —

Precipitated by potassium bichromate from tolerably dilute solutions of the hydrochloride. Recrystallised from water, it appears in orange-yellow needles.

Picrate of Amidacetonnaphthalide, $\begin{array}{c} \text{NH.C}_2\text{H}_5\text{O} \\ \text{C}_{10}\text{H}_6 \\ \text{NH}_2.\text{C}_6\text{H}_3(\text{NO}_2)_3.\text{OH} \end{array}$. — Precipitated by picric acid from dilute solutions of the hydrochloride.

Crystallises from boiling water in beautiful yellow needles.

Naphthylenediamine, $\begin{array}{c} \text{NH}_2 \\ \text{C}_{10}\text{H}_6 \\ \text{NH}_2 \end{array}$. — Obtained by boiling hydrochloride of

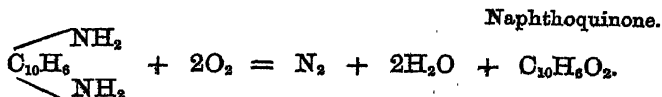
amidoacetonnaphthalide with dilute sodium hydrate solution, whereby the acetyl-group in the former suffers decomposition.

Naphthylenediamine-hydrochloride, $\begin{array}{c} \text{H}_2 \\ \text{N} \\ \text{C}_{10}\text{H}_6 \\ \text{N} \\ \text{H}_2 \\ \text{HCl} \end{array}$. — When the acid solu-

tion of amidoacetonnaphthalide is evaporated and crystallised, this body remains in the mother-liquors, from which it may be precipitated by strong hydrochloric acid.

As no difference could be remarked between the salts of naphthylenediamine thus obtained and those obtained by direct reduction of α -nitro-naphthylamine with tin and hydrochloric acid, it is concluded that the former are α -compounds.

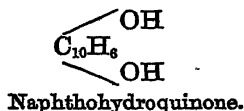
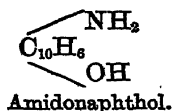
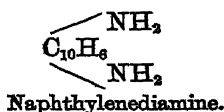
Naphthoquinone, $\text{C}_{10}\text{H}_6\text{O}_2$. — A solution of the hydrochloride of the α -naphthylenediamine was introduced into a large retort, with inverted condenser and drop-funnel containing a one or two per cent. aqueous chromic acid solution. This was gradually allowed to drop into the boiling contents of the retort. The yield is from 50 to 60 per cent. The quinone distils over in the vapour of water and crystallises in yellow prisms, which may be purified by recrystallisation from alcohol. The body is soluble in ether, alcohol, and glacial acetic acid; slightly soluble in water, and easily volatile in the vapour of water; melts at 125° ; when obtained as above, it was found to agree in properties, &c., with the naphthoquinone obtained by Groves. Groves uses a concentrated chromic acid solution and gets a very small yield of naphthoquinone. The author uses at most a one per cent. solution and obtains a purer and more abundant product. The reaction is as follows:—



Naphthoquinone was now treated with a large excess of nitric acid and heated on the water-bath to dryness. The white crystalline mass on sublimation yielded needles of phthalic acid, melting at 129° . This

teaches that both oxygen atoms in naphthoquinone belong to the same benzene group.

α- and β-Nitronaphthols.—As it is yet uncertain whether several phenylenediamines may not be capable of yielding quinones, the attempt was made, for the purpose of fixing the constitution of naphthoquinone, to find another method of preparing this body. Nitronaphthol obtainable from nitracetonaphthalide was converted into amidonaphthol, which forms a link between naphthylenediamine and naphthohydroquinone, and must therefore be convertible into naphthoquinone :



As already mentioned, nitracetonaphthalide boiled with sodium hydrate solution yields a product consisting of *α*-nitronaphthol melting at 164°, and containing also a small quantity of *β*-nitronaphthol melting at 128°.

The two are easily separated, the latter being with difficulty soluble in alcohol; the mixture is therefore extracted with cold spirit of wine, and the residue recrystallised. The *β*-nitronaphthol (m. p. = 128°) crystallises thus in long, narrow leaflets. Better still, the two isomerides may be separated by boiling water, in which the low-melting isomeride is slightly soluble, whereas the high-melting one is very soluble. The solution on cooling yields a mass of yellow needles melting at 164°. A second recrystallisation renders the products quite pure.

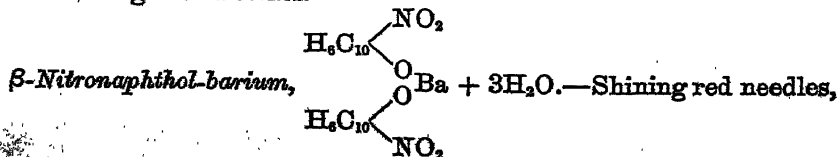
α-Nitronaphthol, $\text{H}_5\text{C}_{10} \begin{array}{l} \diagup \text{NO}_2 \\ \diagdown \text{OH} \end{array}$.—Easily soluble in alcohol and glacial

acetic acid. Crystallises in fine-tangled needle-shaped crystals. In recrystallising from water, what remains dissolved in the mother-liquors is almost completely separated by addition of a few drops of hydrochloric acid. Melting point 164°.

β-Nitronaphthol, $\text{H}_5\text{C}_{10} \begin{array}{l} \diagup \text{NO}_2 \\ \diagdown \text{OH} \end{array}$.—Melting point 128°. Narrow greenish-

yellow leaves, sparingly soluble in dilute alcohol, still less soluble in water.

β-Nitronaphthol-ammonium.—Crystallises from hot, aqueous solutions in orange-red needles.



which at 110° lose water and become brownish-red.

α -Amidonaphthol-hydrochloride, $\text{H}_6\text{C}_{10} \begin{array}{l} \text{NH}_2\text{HCl} \\ \text{OH} \end{array}$.— α -Nitronaphthol

was treated with tin and hydrochloric acid, when the crystallised stannous chloride was obtained. This was dissolved in water, the tin thrown down by sulphuretted hydrogen, the solution filtered and concentrated, and the hydrochloride precipitated by dry hydrochloric acid gas. The salt forms white needles and is very soluble in water. Its solution colours pine-wood orange, and the damp salt soon becomes violet. In a large number of reactions the α -compound always gives naphthoquinone, whilst the β -compound does not furnish a trace.

β -Amidonaphthol hydrochloride.—Prepared like the α -compound. It crystallises in broad, white leaflets. Its solution also reddens pine wood. Shaken up with air and alkalis, it becomes of a grass-green colour. The α -compound becomes of a dirty green, soon changing into yellow.

β -Amidonaphthol picrate, $\text{H}_6\text{C}_{10} \begin{array}{l} \text{NH}_2 \\ \text{OH} \end{array} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$, is precipitated

from dilute solutions of the hydrochloride by picric acid as a yellow crystalline powder.

Conversion of α - and β -Nitronaphthol into Dinitronaphthol.—It has been already shown that in α -nitronaphthol (164°) both the NO_2 and OH groups are in the α -position and exist in one and the same benzene-group. (Proved by the oxidation of naphthoquinone to phthalic acid.)

So far with β -nitronaphthol, only the position of the OH group (α) has been determined. It might be expected that the NO_2 group would exist in the same benzene group, whereby, on account of the isomerism of the α -nitronaphthol, only one of the β -positions could be taken up. Both possibilities were demonstrated if β -nitronaphthol could be converted into the already known dinitronaphthol. This was actually effected by boiling the solution of β -nitronaphthol in alcohol with double the calculated quantity of nitric acid theoretically required. On cooling the dinitro-compound crystallises out in prismatic needles, having the appearance of dinitronaphthol and melting at 138° . Confirmed by analysis.

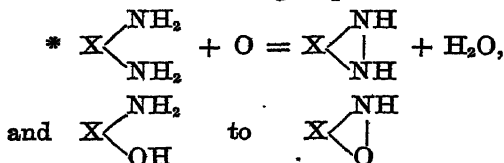
Calcium-dinitronaphthol, $\text{C}_{10}\text{H}_5(\text{NO}_2)_2\text{O} \begin{array}{l} \text{O} \\ \text{O} \end{array} \text{Ca} + 4\text{H}_2\text{O}$.—The salt is

orange-red, but becomes scarlet when deprived of its water of crystallisation.

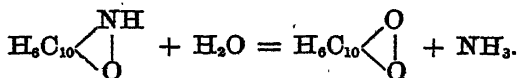
The identity of the dinitronaphthol obtained from the β -nitronaphthol with the known α -dinitronaphthol was placed beyond doubt by its conversion in phthalic acid after several evaporations on the water-bath with nitric acid.

Theoretical considerations of the foregoing.—It has been shown that α -nitronaphthylamine, by replacement of NH_2 by H , gives ordinary α -nitronaphthalene. α -Nitronaphthol can be formed from this same nitronaphthylamine. The nitro-group in this α -nitronaphthol must therefore be in the α position, whilst the hydroxyl-group, which represents the amido-group of the α -naphthylamine, takes up an α position.

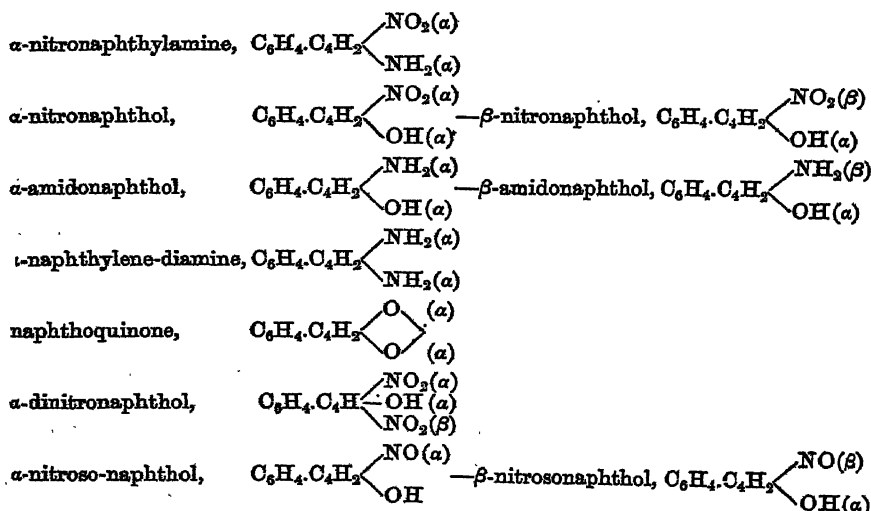
For this reason also both amido-groups of the α -naphthylene diamine and both substituents in the α -amidonaphthol are in α positions. The formation of naphthoquinone from the two naphthylene diamines by oxidation is easily explained as an interchange, no alteration in position of the substituents taking place. The oxidation in the next place only converts the amido- into imido-groups.



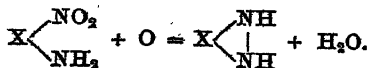
By reaction with water the imidogen groups then take up an atom of oxygen, *e.g.*,



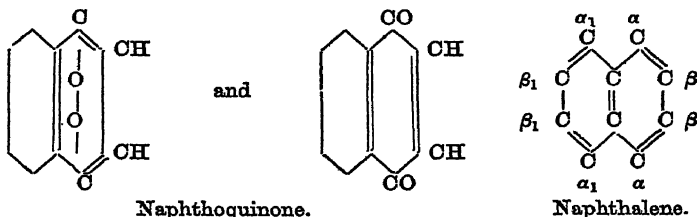
When α -amidonaphthol is treated with nitrous acid, the amido group is replaced by hydroxyl, and naphthohydroquinone is produced, which in presence of nitrogen oxides passes into naphthoquinone. The oxygen-atoms of naphthoquinone must therefore be in α positions. The oxidation of naphthoquinone to phthalic acid teaches further, that both the above α positions must belong to one and the same benzene group. The compounds so far discussed are formulated as follows:—



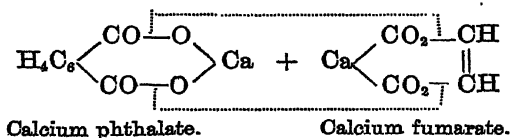
* *Note by Abstractor.*—The above equation in the *Annalen*,⁷ p. 254, appears to contain a misprint. It stands thus—



Naphthoquinone is not regarded as an intermediate member between benzene-quinone and anthraquinone so much as a body very closely related to benzene-quinone, two very similar classes of compounds springing from these two bodies—naphthoquinone and benzene-quinone. The two methods of regarding naphthoquinone are expressed as follows :—



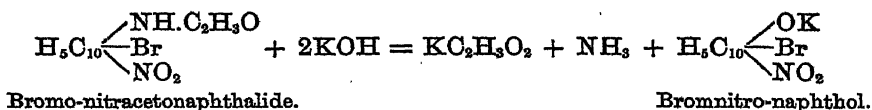
The latter formula would make it appear conceivable that naphthoquinone could be formed from phthalate and fumarate of calcium, according to the following scheme :—



By heating a mixture of calcium phthalate and fumarate together, a completely negative result was, however, obtained, an oil being obtained in which no naphthoquinone could be discovered.

The Isomeric β -naphthylamine.—The β -mono-substitution products of naphthalene, with the exception of the sulpho-acid, are not directly derived from naphthalene, but from the sulpho-acid. Hence those members of the group not derivable from the sulpho-acid have hitherto not been prepared. The attempt has been made to prepare some of the more important of these, and thus to complete the group and obtain clearer theoretical views.

Bromonitracetonaphthalide was boiled with potash, with the following results :—



Bromonitracetonaphthalide is obtained by nitrating bromacetonaphthalide; it is therefore known that the acetamide group as well as the bromine occupies the α -position. After the entrance of the nitro group all three substituents are contained in the same benzene group: hence the nitro-group must occupy a β -position, the two α -positions being occupied already. When pure acetonaphthalide is treated with bromine under carbon disulphide, bromacetonaphthalide is obtained, but an altogether new substance remains in the mother-liquors.

Bromonitronaphthylamine, $\text{H}_5\text{C}_{10} \begin{array}{l} \nearrow \text{Br} \\ \text{---} \text{NO}_2 \\ \searrow \text{NH}_2 \end{array}$, forms long crystals, melting at 200° ; dissolves easily in concentrated sulphuric acid; and the saturated solution after some time deposits colourless needles of the sulphate.

Bromonitronaphthylamine repeatedly evaporated on the water-bath with nitric acid (half strength) becomes oxidised, phthalic acid being formed. This decomposition proves that bromonitronaphthylamine has

the formula $\text{C}_6\text{H}_4 \cdot \text{HC}_4 \begin{array}{l} \nearrow \text{NH}_2(\alpha) \\ \text{---} \text{Br}(\alpha) \\ \searrow \text{NO}_2(\beta) \end{array}$.

Bromonitronaphthalene, $\text{H}_5\text{C}_{10} \begin{array}{l} \nearrow \text{NO}_2 \\ \text{---} \text{Br} \end{array}$. The previous compound is dis-

solved in concentrated sulphuric acid, and water gradually added till the solution changes from dark red to bright yellow, with separation of a precipitate. Into the well cooled solution nitrous acid is then passed to saturation, and afterwards gradually double the volume of absolute alcohol is added. The powerful action taking place is moderated by cooling, and the nitrous ether is then driven off on the water-bath. The bromonitronaphthalene is thus obtained in reddish needles, which are recrystallised from alcohol, and are then yellowish-white, and melt at $131\text{--}132^\circ$, dissolve easily in alcohol and ether, and sublime readily.

The constitution is $\text{C}_6\text{H}_4 \cdot \text{H}_2\text{C}_4 \begin{array}{l} \nearrow \text{NO}_2(\beta) \\ \text{---} \text{Br}(\alpha) \end{array}$.

β -Naphthylamine, $\text{C}_{10}\text{H}_7\text{NH}_2$.—It was not found possible to remove the bromine atom from bromonitronaphthalene without simultaneous reduction of the nitro group. By reduction of bromonitronaphthalene with granulated tin and dilute hydrochloric acid, the β -naphthylamine was obtained. It crystallises in nacreous plates, melting at 112° (the α -compound melts at 50°). It has not the characteristic odour of the α -naphthylamine. Neither with ferric chloride, chromic acid, chloride of lime, nor alcoholic solution of nitrous acid and hydrochloric acid, is the tint obtained which characterises the α -base. The great differences of melting point and crystallisation observed in the α - and β -naphthylamines is also observed quite analogously with the corresponding naphtholes. A useful indication for distinguishing between the compounds of the α - and β -groups is the tendency possessed by the members of the former to exhibit colour reactions, a property quite wanting in those of the latter.

β -Naphthylamine Hydrochloride, $\text{C}_{10}\text{H}_7\text{NH}_2 \cdot \text{HCl}$.—Colourless plates, very easily soluble in water and alcohol.

β -Naphthylamine Platinochloride, $(\text{C}_{10}\text{H}_7\text{NH}_2 \cdot \text{HCl})_2\text{PtCl}_4$.—Yellow plates, soluble in cold water.

β -Naphthylamine Sulphate, $(\text{C}_{10}\text{H}_7\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$.—Not easily soluble, so that sulphuric acid precipitates it from cold dilute solutions of the chloride. From hot water it crystallises in beautiful plates. The α -salt is quite soluble. This difference of solubility was used with considerable success as a means of separating the isomeric salts.

β-Naphthylamine Picrate.—Crystallises from hot water in long yellow needles, soluble in alcohol, and melting at 195° with decomposition.

β-Acetonaphthalide, $C_{10}H_7-N \begin{matrix} H \\ \diagup \\ C_2H_3O \end{matrix}$.—Melting point 132°. Shining plates, resembling benzoic acid.

Conversion of β-naphthylamine into other β-derivatives.—The object of this research was to determine directly the β-position of the newly discovered β-naphthylamine.

β-Naphthol, $C_{10}H_7(OH)$, from β-naphthylamine.—The latter was dissolved in concentrated sulphuric acid, and water added till a thick paste was formed, and then, after well cooling, nitrous acid was passed through. Addition of alcohol and ether threw down the β-diazonaphthalene sulphate in fine needles. From the cooled filtrate reddish plates separated, which were obtained white by solution in dilute soda-ley, precipitation with acid, and boiling with animal charcoal. Melting point = 122°. With chloride of lime and ferric chloride the violet colour characteristic of α-naphthol did not appear, but only a faint yellowish tint.

β-Bromonaphthalene, $C_{10}H_7.Br(\beta)$.—A comparison of the melting points of the respective members of the α- and β-groups shows that those of the former are considerably higher than those of the latter. It was therefore considered probable that the β-bromonaphthalene, in contrast to the liquid α-compound, would probably be solid at ordinary temperatures. To prepare this body, the solution of the diazo-compound of β-naphthylamine was treated with a solution of bromine in bromine water. Orange-yellow flocks, consisting of groups of minute needles, then separated. This body is a perbromide, which slowly decomposes on drying. By boiling it with alcohol, and adding water, a semi-solid body is obtained, which must be pressed in blotting paper, and then distilled with steam. The distillate recrystallised from alcohol, yields colourless plates of the β-bromonaphthalene, melting at 68°, and easily soluble in alcohol, ether, chloroform and benzol.

β-Chloronaphthalene.—Diazodaphthalene sulphate was boiled with strong hydrochloric acid. The crystalline mass obtained on cooling and standing was pressed, dissolved in alcohol, and then water added till turbidity began to appear; white plates crystallised out. Melting point = 61°.

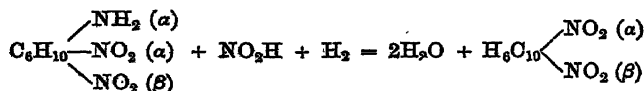
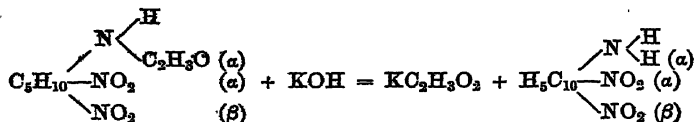
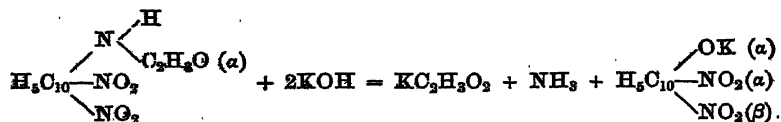
The following is a list of *melting points* of the respective members of the α- and β-groups, where it is observable that 12 in the β-group melt at higher temperatures than their neighbours in the α-group.

	α-Group.	β-Group.
$C_{10}H_7.Cl$	liquid	56° (61, 53 ?)
$C_{10}H_7.Br$	liquid	69°
$C_{10}H_7.Cy$	37°	66°
$C_{10}H_7.OH$	94°	122°
$C_{10}H_7.OC_2H_5$	liquid	33°
$C_{10}H_7.OC_2H_3O$	liquid	60°

	α -Group.	β -Group.
$C_{10}H_7.SH$	liquid	137°
$C_{10}H_7.NH_2$	50°	112°
$C_{10}H_7.NH.C_2H_5O$..	159°	132°
$C_{10}H_7.CO_2H$	161°	181°
$C_{10}H_7.COCl$	liquid	43°
$C_{10}H_7.CONH_2$	204°	192°
$C_{10}H_7.CO.C_6H_5$	75°	82°
$C_{10}H_7.SO_2Cl$	66°	76°

α β -Dinitronaphthalene, $H_5C_{10} \begin{matrix} \swarrow NO_2(\alpha) \\ \searrow NO_2(\beta) \end{matrix}$. — Dinitracetonaphthalide

was boiled with potassium hydrate, and thus converted into α -dinitronaphthol, the acetyl group being thus removed. The amido group in the dinitronaphthylamine was then replaced by hydrogen, so that a dinitronaphthalene remained, in which the position of the nitro-groups is the same as in the dinitronaphthol. The reactions are as follows:—



Dinitroacetophthalide, $H_5C_{10} \begin{matrix} \swarrow N \begin{matrix} \nearrow H \\ \searrow C_2H_5O \end{matrix} \\ \searrow NO_2 \end{matrix}$, forms long yellow needles, melting at 247°.

α -Dinitronaphthol, $H_5C_{10} \begin{matrix} \swarrow OH \\ \searrow NO_2 \end{matrix}$. — By boiling the above with sodium hydrate solution the aceto-compound is decomposed, with evolution of ammonia, and acids added to the filtered liquid precipitate yellow flocks, which by recrystallisation give the completely pure crystallised body. The sodium, calcium, and barium salts were very similar to those of the α -dinitronaphthol.

Dinitronaphthylamine, $H_5C_{10} \begin{matrix} \swarrow NH_2 \\ \searrow NO_2 \end{matrix}$. — Dinitroacetophthalide was heated in sealed tubes for three hours with alcoholic ammonia to 140°. The contents of the tube were recrystallised from alcohol. Lemon-yellow needles, melting at 235°.

Dinitronaphthalene, $\text{H}_6\text{C}_{10} \begin{matrix} \nearrow \text{NO}_2(\alpha) \\ \searrow \text{NO}_2(\beta) \end{matrix}$.—*Dinitronaphthylamine* was dis-

solved in concentrated sulphuric acid, and precipitated with water as a thick paste. Nitrous acid was then passed through the solution till it became clear, and four to five times the volume of alcohol was gradually added. About half of the alcohol was then driven off on the water-bath, and water added to precipitate the compound. This, by repeated extraction with boiling dilute soda, and recrystallisation from dilute alcohol, with addition of animal charcoal, was obtained pure. Light yellowish, almost colourless needles, melting at 144° . This dinitronaphthalene must therefore have a different constitution from the other two, melting respectively at 170° and 210° .

W. S.

Studies in the Anthraquinone-group. By CARL LIEBERMANN (*Liebig's Annalen*, clxxxiii, 145—224).—Some portions of these researches, by the author, in conjunction with other chemists, have already appeared in abstract in this Journal, but it appears desirable, nevertheless, to abstract the present paper as it stands.

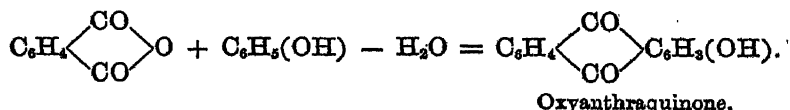
OXYANTHRAQUINONE.—This substance, one of the bye-products in the manufacture of alizarin, was first analysed by the author, who assigned to it the formula $\text{C}_{14}\text{H}_8\text{O}_3$. It was at one time thought to be identical with Schunck's anthraflavic acid, but later researches have shown that this is a distinct body. Monoxanthraquinone is formed from anthraquinone-monosulphonic acid, and is converted by oxidation into alizarin; whereas anthraflavic acid is formed from a disulphonic acid, and is converted by fusion with potash into an isomeric purpurin (flavopurpurin).

Oxyanthraquinone crystallises from hot alcoholic solution in yellow laminæ or needles, and from glacial acetic acid in long silky needles. It does not melt at 285° , and sublimes at a higher temperature in lemon-yellow laminæ. When heated with zinc-dust, it yields anthracene, and when warmed with fuming nitric acid, large quantities of phthalic acid. Its formula, deduced from numerous analyses, is $\text{C}_{14}\text{H}_8\text{O}_3$.

Oxyanthraquinone is very soluble in water. It dissolves in alkalis, forming reddish-yellow solutions; also in lime and baryta-water. Its solution in hot strong baryta-water deposits red crystals, which, after drying at 130° , have the composition represented by the formula $(\text{C}_{14}\text{H}_7\text{O}_3)_2\text{Ba}$. It is insoluble in acidulated water.

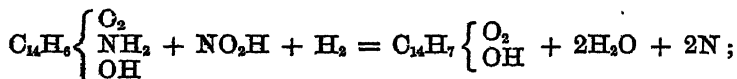
The *acetyl-compound* of oxyanthraquinone crystallises from alcohol in small yellowish, matted needles, having the formula $\text{C}_{14}\text{H}_7(\text{C}_2\text{H}_5\text{O})\text{O}_3$.

Oxyanthraquinone has also been obtained by several other reactions. Thus, Baeyer and Caro obtained it by heating together phthalic anhydride, phenol, and strong sulphuric acid:

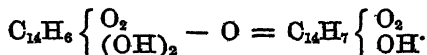


Oxyanthraquinone.

Troschka and the author obtained it by the action of nitrous acid on an alcoholic solution of alizarinamide :



and it has been obtained by Fischer and the author by heating an alkaline solution of alizarin with stannous chloride :



Chrysophanic Acid and Emodin.—These substances occur together in rhubarb-root. They are extracted from the root by benzene, in which, however, the emodin is less soluble than the acid. The two substances are separable by means of soda-ley, which dissolves emodin with blood-red colour, but leaves chrysophanic acid undissolved.

Emodin crystallises best from glacial acetic acid in silky orange-red needles, which melt at 245—250°, and dissolve with cherry-red colour in weak ammonia. Its composition, as determined by analysis, agrees with the formula $C_{15}H_{10}O_5$.

Acetyl-emodin.—Emodin heated to 150—160° with acetic anhydride in sealed tubes forms with it a compound which crystallises from excess of the anhydride in yellow needles, and from glacial acetic acid in laminae, melting at 179—180°. Its composition agrees with the formula of *monacetyl-emodin*, $C_{16}H_8(C_2H_3O)_2O_5$.

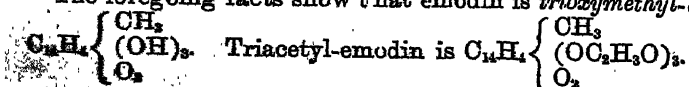
A second acetyl-compound, formed by heating emodin to 175° with acetic anhydride, crystallises from glacial acetic acid in yellow needles, melting at 190°. Its composition is that of *triacetyl-emodin*, $C_{18}H_7(C_2H_3O)_3O_5$.

Neither of these compounds is dissolved or coloured by ammonia, but they are easily decomposed by potash, emodin being re-produced.

Methylantracene from Emodin.—Emodin distilled with zinc-dust yields a hydrocarbon, which, from its behaviour with oxidising agents, is proved to be a mixture of anthracene and methylantracene. The hydrocarbon has not been actually separated into these substances; but when it is oxidised with chromic and acetic acids, it is converted into anthraquinone and the following substance:—

Anthraquinone-carbonic Acid, $C_{14}H_7O_2.CO_2H$.—This body, formed as just stated, is deposited from alcohol in small indistinct crystals agreeing in composition with the formula $C_{15}H_5O_4$. It melts at 280°. Its reaction with zinc-dust in alkaline solution resembles that of anthraquinone, but the colour produced is more yellow than red. It sublimes at a high temperature, yielding a sublimate resembling anthraquinone and soluble in ammonia. When heated with sulphuric acid, it forms a sulphonic acid, which, by fusion with potash, yields alizarin.

The foregoing facts show that emodin is *trioxymethyl-anthraquinone*,



Methylanthracene from Chrysophanic Acid.—Chrysophanic acid yields by distillation with zinc-dust a hydrocarbon very closely resembling that obtained from emodin, and melting at 199–200°. The hydrocarbon yields by oxidation anthraquinone-carbonic acid in every respect similar to the acid described above.

Methylanthraquinone.—Methylanthracene is converted by oxidation with nitric acid into methylanthraquinone, a body subliming and crystallising from alcohol in yellow needles.

Hence it appears that the hydrocarbon from which chrysophanic acid is derived is methylanthracene, and the formula of chrysophanic acid must, therefore, be written $C_{15}H_{10}O_4$, and not $C_{14}H_8O_4$, as formerly proposed by Graebe and the author.

Acetylchrysophanic Acid.—This body, as prepared by the author, forms small yellow laminæ, melting at 202–204°, and agreeing in composition with the formula $C_{15}H_8(C_2H_3O)_2O_4$.

Chrysophanic acid must, therefore, be regarded as *methylidioxy-anthraquinone*, $C_{14}H_5 \begin{Bmatrix} CH_3 \\ (OH)_2 \\ O_2 \end{Bmatrix}$. It stands in precisely the same relation to emodin as does alizarin to purpurin.

NITROCHRYSOPHANIC ACID, CHRYSAMMIC ACID, AND CHRYSAZIN.—The substance formed by the action of nitric acid on chrysophanic acid was at one time thought to be identical with chrysammic acid, but later researches have shown that such is not the case.

Tetranitrochrysophanic Acid.—Chrysophanic acid dissolves easily in nitric acid, and is converted thereby into a substance crystallising in yellow needles, and agreeing in composition with the formula $C_{15}H_4(NO_2)_4O_4$. This body is nearly insoluble in cold, and sparingly soluble in boiling water. It is a strong acid, and forms salts differing very considerably from those of chrysammic acid. The nitro-chrysophanates are much more easily soluble in water than the chrysammates; they do not exhibit the metallic lustre of the latter; and they crystallise badly.

Hydrochrysammide.—This body, formed by the action of reducing agents on chrysammic acid, was discovered by Schunck, who assigned to it the formula $C_{14}N_{12}N_4O_8$. The author's analyses of the substance, as obtained by the reducing action of potassium sulphhydrate, lead however to the formula $C_{14}H_{12}N_4O_4$, according to which hydrochrysammide is to be regarded as a tetramido-compound, of the formula $C_{14}H_4(NH_2)_4O_4$.

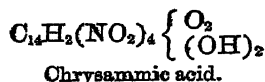
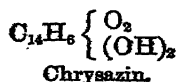
Chrysazin.—This name has been given by the author to a compound obtained by treating a solution of hydrochrysammide in sulphuric acid with nitrous acid, and boiling the resulting diazo-compound with alcohol. The product, when pure, forms reddish-brown shining needles or yellow laminæ, both melting at 191°. It dissolves sparingly in alcohol, chloroform, glacial acetic acid, and ether, and in strong sulphuric acid with red colour. Caustic alkalis dissolve it easily in the cold; the carbonates only on warming: calcium and barium salts produce in these solutions red precipitates of the corresponding chrysazin salts. In the alcoholic solution basic lead acetate produces a red precipitate. Chrysazin distils when heated, and afterwards

solidifies in long orange-red needles. It yields on analysis numbers agreeing with the formula $C_{14}H_8O_4$.

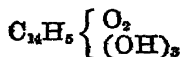
The formation of chrysazin from hydrochrysammide is remarkable as being the first instance of the replacement by hydrogen of *four* amido-groups in the same molecule by means of nitrous acid. In accordance with this reaction, hydrochrysammide is to be regarded as tetramidochrysazin, and chrysammic acid as tetranitrochrysazin.

Constitution of Chrysazin.—Chrysazin being formed from chrysammic acid by the replacement of nitro-groups by hydrogen, and chrysammic acid containing two hydroxyl-groups, as shown by the composition of its salts, it follows that chrysazin must also contain two hydroxyl-groups. As a derivative of anthracene, it must, therefore, be a dioxanthraquinone, $C_{14}H_8O_4 = C_{14}H_6 \left\{ \begin{smallmatrix} O_2 \\ (OH)_2 \end{smallmatrix} \right.$; that is, an isomeric alizarin. This view of its constitution is confirmed by the composition of the following substance.

Acetylchrysazin.—Chrysazin heated to 170° with excess of acetic anhydride forms yellow laminæ of a compound melting at $226-230^\circ$, subliming in small laminæ, and agreeing in composition with the formula $C_{14}H_6(C_2H_3O)_2O_4$. The substance is, therefore, diacetylchrysazin. Hence the constitution of chrysazin, hydrochrysammide, and chrysammic acid, may be expressed thus:—



Oxychrysazin.—Chrysazin, when fused with potash, yields a body agreeing in composition with the formula $C_{14}H_6O_5$. This product is sparingly soluble in alcohol. It dissolves in alkalis with violet colour, also in carbonates in the cold, and gives with baryta-water an insoluble blue precipitate. As a dye, it produces brilliant tints intermediate between those of alizarin and purpurin. It forms an acetyl-compound crystallising in yellow needles, which melt at $192-193^\circ$, and have the composition indicated by the formula $C_{14}H_6(C_2H_3O)_3O_5$. Oxychrysazin is, therefore, represented by the constitutional formula—

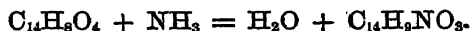


It is isomeric, but not identical with purpurin and isopurpurin.

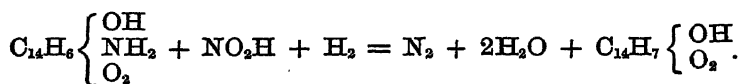
Nitrochrysazin.—Chrysazin, when heated in the water-bath with an excess of fuming nitric acid, yields a substance agreeing in composition with the formula $C_{14}H_2(NO_2)_4O_4$. The substance is, consequently, tetranitrochrysazin. It is identical in composition, crystalline form, and optical properties, with chrysammic acid. Moreover, its potassium, calcium, magnesium, and barium salts are identical with those of chrysammic acid.

AMIDO-COMPOUNDS OF THE OXYANTHRAQUINONES.—*Alizaramide.*—This substance is formed on heating a solution of alizarin in strong aqueous ammonia to 200° for some hours in sealed tubes. It crystallises from

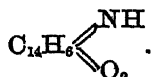
boiling alcohol in fine brown needles, having a green metallic lustre and agreeing in composition with the formula $C_{14}H_5NO_3$:



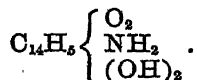
Alizaramide is soluble with yellow colour in strong sulphuric acid, and slightly in hot strong hydrochloric acid. It forms violet-red solutions in alkalis and baryta-water, and is not decomposed by boiling these solutions, nor by boiling dilute hydrochloric acid. When fused with potash, it yields alizarin. On boiling it with barium carbonate, a barium compound is formed, having the composition indicated by the formula $(C_{14}H_5NO_2)_2Ba$, whence it follows that the group HO in alizarin is replaced by NH_2 in the amide. This is shown to be the case also by the action of nitrous acid on the amide in alcoholic solution, whereby oxyanthraquinone is produced:



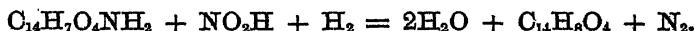
Alizarimide.—When ammonia is heated with a much larger proportion of alizarin than in the foregoing process, the chief product is a crystalline substance, which dissolves with violet colour in alcohol and crystallises therefrom in reddish-brown needles. Its composition is represented by the formula $C_{14}H_{16}N_2O_2$. This substance is the ammonia-compound of alizarimide, $C_{14}H_7NO_2$. The latter body is isolated by boiling the ammonia-compound dissolved in alcohol with a little hydrochloric acid. It crystallises in reddish-brown needles. Its constitution may be expressed by the formula:



Purpuramide.—This substance is formed by the action of ammonia on purpurin in the same manner as alizaramide. It crystallises in brown needles having a green metallic lustre. Its solution in alkalis is much redder than that of alizarinamide. Analysis shows it to have the composition represented by the formula $C_{14}H_5NO_4$. Its constitutional formula is



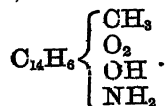
Purpuramide is decomposed by nitrous acid in precisely the same manner as alizaramide, *purpuroanthin* being formed, thus:



Purpuroanthin has hitherto been regarded as an isomeric alizarin, and this view of its constitution is confirmed by the author's researches. When distilled with zinc-dust, it yields anthracene. Its *acetyl-compound* forms fine yellow needles, melting at $183-184^\circ$, and agreeing in composition with the formula $C_{14}H_5(OC_2H_3O)_2O_2$. When heated

with ammonia, it yields an *amide*, $C_{14}H_9NO_3$, crystallising in brown needles, and closely resembling purpurinamide.

Amidochrysophanic Acid.—This body is formed, together with an ammonia-compound ($C_{15}H_{11}NO_3NH_3$), by heating chrysophanic acid with strong ammonia to 200° in sealed tubes. It crystallises from alcohol in small brown laminæ, analysis of which leads to the formula $C_{15}H_{11}NO_3$. Its constitution is represented thus:

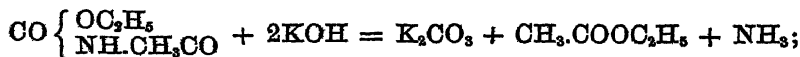


Another product of the action of ammonia on chrysophanic acid is obtained when a larger proportion of the acid is employed, and the temperature is not allowed to rise above 150° . The product gives on analysis numbers agreeing with the formula $C_{15}H_{13}N_2O_2$, and accordingly it may be either a diamidochrysophanic acid, $C_{15}H_9 \left\{ \begin{array}{l} O_2 \\ (NH_2)_2 \end{array} \right.$, or

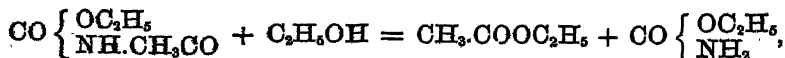
an ammonia-compound of chrysophanic imide, $C_{15}H_9 \left\{ \begin{array}{l} O_2 \\ NH.NH_3 \end{array} \right.$, analogous to the alizarin-compound described above. Its constitution is not yet definitely made out. When boiled with acetic anhydride, it forms a compound which crystallises in fine violet needles, having a metallic lustre and agreeing in composition with the formula $C_{15}H_9O_2N(C_2H_5O)$. J. R.

Action of Acetyl Chloride and of Benzoyl Chloride on some Amides. By ALFRED KRETSCHMAR (*Chem. Centr.*, 1876, 233—240).—The object of this research was to supplement the labours of Zinin, of Moldenhauer, of Nencki, and of Pike, with regard to the action of the chlorides of acid radicles on bodies resembling urea.

With urethane, $CO \left\{ \begin{array}{l} OC_2H_5 \\ ONH_2 \end{array} \right.$, at 110° , *acetyl urethane*, $CO \left\{ \begin{array}{l} OC_2H_5 \\ NH.CH_3CO \end{array} \right.$, was formed by the action of acetyl chloride. The product was extracted by means of ether, in which, as well as in alcohol and water, it dissolves; it crystallises in radiated groups of silky needles, and melts at $77-78^\circ$. It has a neutral reaction. By the action of cold alcoholic potash it is decomposed thus:—



and by alcoholic ammonia thus:—

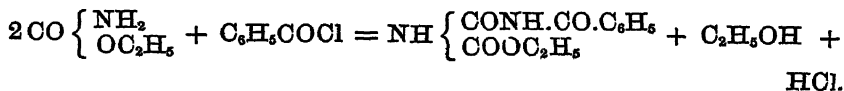


the ammonia taking no part in, but nevertheless being indispensable to the reaction, for the decomposition does not take place with alcohol alone.

In a similar manner, *acetyl-oxamethane*, $CO.OC_2H_5$, $CONH.CH_3CO$, was formed;

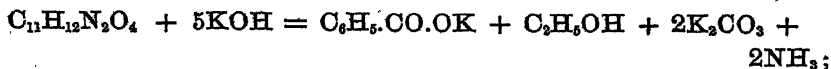
it consists of a syrup which crystallises with great difficulty, but after once assuming the crystalline form, is not difficult to recrystallise. It melts at 54° , and is easily soluble in alcohol and in ether, but scarcely dissolves in water. Its behaviour with potash and with ammonia is perfectly analogous to that of urethane, acetate and oxalate of calcium, alcohol, and ammonia being the products of the first reaction, and urea, acetamide, and alcohol being obtained by the second.

The action of *benzoyl chloride* on urethane differs from that of acetyl chloride. The action begins at about 140° , and is over at 160° , torrents of hydrochloric acid escaping. The product dissolves almost completely in boiling alcohol, leaving a small residue of ammonium chloride, and as the alcohol cools it is found to be filled with thin needles matted together. Too large an amount of substance should not be used at one operation—15 grams of urethane and 23 grams of benzoyl chloride were used by the author—else by-products are formed in large quantity. The product had the formula $C_{11}H_{12}N_2O_4$, and from its decomposition with potassium hydroxide and with ammonia, was proved to be *benzoyl-allophanic ether*. The reaction by which it is formed is this :—

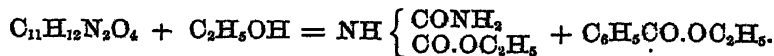


It is almost insoluble in cold alcohol, in ether, and in water. It melts at about 163° , and is very easy to crystallise.

On boiling it with alcoholic potash, the following reaction takes place :—



and in sealed tubes, with alcoholic ammonia at 100° , complete decomposition ensues, allophanic and benzoic ethers being formed, thus :—



As before, ammonia induces, but does not participate in the reaction.

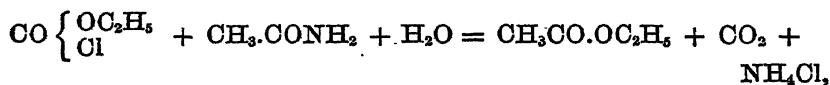
At 210° this body decomposes thus :—



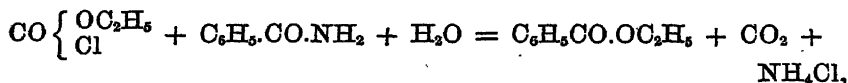
cyanuric acid and benzoic ether being the products.

Benzoyl chloride acts on oxamethane at 160 — 170° , but that temperature appears to be too high for the existence of benzoyl oxamethane. Complete decomposition ensues, carbonic anhydride and hydrochloric acid being evolved.

An attempt, which proved unsuccessful, was made to prepare acetyl- and benzoyl-urethane and -oxamethane by treating chlorocarbonic ether and ethyloxalyl chloride with acetamide and benzamide respectively. The reactions are probably these, although the author endeavoured to have perfectly dry substances :—



and



and the products are still more numerous in the case of ethylloxalyl chloride, but point to similar reactions.

An attempt was also made to substitute more than two atoms of hydrogen in urea by treating ethylbenzoyl-urea with acetyl chloride. The reaction began at the ordinary temperature, and the product, on crystallisation from alcohol, proved to be identical with Zinin's benzoyl-urea. Benzoyl chloride acts on benzoylethyl-urea when the two bodies are warmed together in the water-bath. The product, on analysis, did not give numbers answering exactly to any formula, but from its behaviour when heated, the author believes it to have consisted chiefly of benzoyl-urea.

W. R.

Thiamides of Monobasic Organic Acids. By A. BRENTHESEN (*Liebigs Annalen*, cxxxiv, 290—320).—The compounds obtained by the union of the nitrils with hydrogen sulphide have been regarded either as sulphuretted amides (thiamides), or merely as addition-products; but as experimental evidence was wanting in order to settle definitely the constitution of this class of bodies, the author has undertaken an investigation of the thiamides.

Phenylacetothiamide or *Thio-alphatolylamide*, $\text{C}_6\text{H}_5.\text{CH}_2.\text{CN}.\text{H}_2\text{S}$.—Hydrogen sulphide has no action on an alcoholic solution of benzyl cyanide, but on adding a small quantity of ammonia, the gas is rapidly absorbed, and the liquid acquires a bright red colour. On concentrating the solution, the thiamide is deposited in thick prisms, or it may be precipitated, along with unaltered cyanide and some phenylacetamide, by the addition of water to the alcoholic solution. On exposing the original alcoholic solution to the air for 14 days it deposited some sulphur, and a substance crystallising in long needles, which are only slightly soluble in alcohol. This compound, which has not yet been examined, melts at 197° , and is formed from the thiamide by the oxidising action of the air in presence of ammonia. The phenylacetothiamide may be easily purified by recrystallisation from alcohol, when it forms colourless plates melting at $97.5\text{--}98^\circ$. The crystals belong to the rhombic system, and the measurements are given.

When phenylacetothiamide is carefully heated at 120° , it decomposes, with evolution of hydrogen sulphide, and leaves nearly pure benzyl cyanide. Heated with dilute hydrochloric acid, the thiamide yields phenylacetic acid, with evolution of hydrogen sulphide, whilst with solution of potassium hydrate it gives a sulphide and benzyl cyanide; with ammonia, phenylacetamide and ammonium sulphide are formed. From what is known of the action of nascent hydrogen on the thiamides, it seemed probable that phenylacetothiamide would yield phenyl-

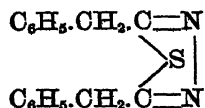
ethylamine, $C_6H_5.CH_2.CH_2.NH_2$, when treated with zinc and dilute hydrochloric acid in alcoholic solution; the principal product, however, was phenylacetic ether, formed by the action of the hydrochloric acid. At the same time a small quantity of a viscous substance of repulsive odour was produced. This compound was also formed by the action of sodium amalgam on the thiamide in presence of acetic acid and water, together with a very small quantity of a basic substance which, from the composition of its platinum salt, seemed to be phenethylamine, $C_6H_5.CH_2.CH_2.NH_2$. On treating the viscous substance above mentioned successively with alcohol, ether, and chloroform, the author succeeded in extracting a compound, $C_{24}H_{27}NS_2$, which crystallises in iridescent, colourless, rhombic plates. It is odourless, and melts at $107.5-108^\circ$. It is but slightly soluble in alcohol or water, more soluble in ether, and readily in chloroform; heated with alcoholic lead acetate, it yields lead sulphide; with potassium hydrate solution it gives ammonia. The author considers it possible that this compound is formed in the manner expressed by the equation—



As the amount of phenethylamine obtained by the action of sodium amalgam on phenylacetothiamide was very small, it seemed probable that a better result might be obtained by the action of reducing agents on benzyl cyanide itself. The cyanide dissolved in alcohol was therefore submitted to the action of zinc and hydrochloric acid for four or five weeks at the ordinary temperature, the greater part of the alcohol removed by distillation, and the unattacked cyanide precipitated by water. The solution containing the zinc chloride was decomposed by sodium carbonate, filtered, neutralised with hydrochloric acid, and concentrated by evaporation, removing the sodium chloride from time to time as it separated. The clear concentrated solution was finally decomposed by sodium hydrate, and the liberated phenethylamine taken up by ether. On evaporation, the ethereal solution left a reddish-brown residue, which soon solidified to a crystalline mass. This was dissolved in dilute hydrochloric acid, and the solution, filtered from a small quantity of a neutral oil, left the impure *hydrochloride*, $C_8H_{11}N.HCl$, on being evaporated under a desiccator. It is exceedingly soluble both in water and in alcohol, but may be purified by crystallisation from dry alcohol, when it forms large colourless plates. Its alcoholic solution is precipitated by ether. The *platinum salt*, $(C_8H_{11}N.HCl)_2PtCl_4$, which crystallises in long hexagonal scales, is but little soluble in boiling water, more readily in hot alcohol. *Phenethylamine* itself, liberated from the hydrochloride by means of sodium hydrate, crystallises in scales which are but slightly soluble in water, very soluble in alcohol, ether, and chloroform. It is a powerful base, possessing a characteristic odour, and readily absorbs carbonic anhydride from the air. It melts at $87-88^\circ$, and sublimes readily. This base may be regarded either as the amine of primary phenethyl alcohol, or as ethylamine, in which one of hydrogen is replaced by the benzene residue C_6H_5 , thus, $CH_3(C_6H_5).CH_2.NH_2$. It is isomeric with xylidine, $C_6H_3(CH_3)_2.NH_2$, with amidoethylbenzene, $C_6H_4(C_2H_5).NH_2$, also with ethylaniline, $C_6H_5.NH.C_2H_5$, and with dimethylaniline, $C_6H_5.NH.(CH_3)_2$.

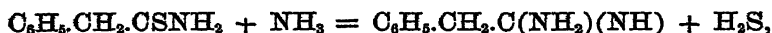
The action of ethyl bromide on a solution of phenethylamine in chloroform, caused the precipitation of *ethylphenethylamine hydrobromide*, $C_8H_9.NH.C_2H_5.HBr$. It is easily soluble in water and in alcohol, crystallising from the latter in large, colourless, rectangular plates. The free base forms small white scales.

The action of iodine on *phenylacetothiamide* in hot alcoholic solution caused the separation of a large amount of sulphur, mixed with a small quantity of an oily body. The latter, by treatment with alcohol and ether, was obtained in the crystalline state, and had the formula $C_{16}H_{14}N_2S$, or—

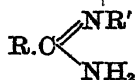


a body analogous to that obtained by Hofmann from benzothiamide by a similar process. It melts at $41-42^\circ$. It is very slightly soluble in water, easily in alcohol, and very readily in ether and chloroform. Treated with zinc and hydrochloric acid in alcoholic solution, it yields a base which has not been further examined.

The author promises, in his next communication, to give full details of the behaviour of phenylacetothiamide and other thiamides with ammonia and amines, merely stating that the action of ammonia on phenylacetothiamide may be represented by the equation—

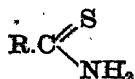


whilst aniline and other primary amines give with benzothiamide or phenylacetothiamide, compounds of the formula—

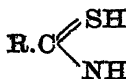


analogous to Strecker's acediamine, the formation of which corresponds with that of guanidines from the sulphureas or thiocarbamides.

A short section then follows on *the constitution of the thiamides*. The action of iodine and of nascent hydrogen on the thiamide excludes the supposition that it is merely an addition-product, so that it is probable that bodies of this class should be represented by one or other of the two formulae—



(I.)



(II.)

Both of these readily permit of an explanation of the action of heat in causing them to split up into the nitril and hydrogen sulphide, and also of the action of nascent hydrogen. As iodine, however, does not act in such a way as to yield the disulphide $[R.C(NH)]_2S_2$, but gives rise to the compound $C_{16}H_{14}N_2S$, the formula I. would seem to be the more probable; this is corroborated by the action of ammonia and the action on the thiamides, which is entirely analogous to the formation

of guanidines from the sulphureas, and will be fully discussed in the next part of the research.

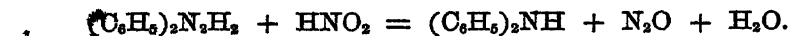
An addendum is appended to this paper on *phenylacetamide*, $C_6H_5.CH_2.CO.NH_2$. Weddige's method of heating benzyl cyanide with potassium sulphide answers well with small quantities (30 grams cyanide) if the heating be continued for several days. The compound may also be prepared by long boiling of a mixture of phenylacetic ether with aqueous alcoholic ammonia, or better by heating to $140-150^\circ$ in sealed tubes. It crystallises in colourless plates or tables, which melt at $155-156^\circ$; slightly soluble in water and ether, more readily in alcohol. On adding a few drops of concentrated hydrochloric acid, to a mixture of phenylacetamide with aldehyde, heat is developed, and the liquid solidifies to a crystalline mass of *ethylidene-phenylacetamide*, $CH_3.CH(NH.CO.CH_2.C_6H_5)_2$, a substance analogous to Nencki's ethylidene-benzamide, and other similar compounds. It crystallises in snow-white needles, which melt at $227-228^\circ$; they are only slightly soluble in water and in ether, more soluble in hot alcohol. This compound, although not acted on by dilute soda solution, readily splits up into aldehyde and phenylacetic ether, when boiled with dilute hydrochloric acid. C. E. G.

Aromatic Hydrazin-compounds. By EMIL FISCHER (*Deut. Chem. Ges. Ber.*, ix, 1840—1845). The author acted upon the nitrosamine (obtained by the action of nitrous acid (KNO_2 and HCl) on diphenylamine) in alcoholic solutions with zinc-dust and glacial acetic acid, and obtained the hydrochloride of the hydrazin base, $(C_6H_5)_2N_2H_2.HCl$. This when acted on by caustic soda gave the hydrazin base as a light yellow oil, not solidifying in a freezing mixture. It is difficultly soluble in water, easily in alcohol and ether; only partly volatile without decomposition, the greater part being decomposed into ammonia, diphenylamine and resinous products; dissolves without alteration in oil of vitriol, forming a deep blue solution. The sulphate and nitrate crystallise from hot solutions in fine white needles, becoming blue on exposure to the air.

Its constitution is best expressed by the formula $(C_6H_5)_2N-NH_2$, thus making it an unsymmetrical substitution-product of the group NH_2-NH_2 . This view not only accounts for all the subsequent reactions, but throws a light on its relations to the isomeric hydrazobenzene. For the formula of the latter being $C_6H_5-NH-NHC_6H_5$, it may evidently be regarded as a derivative of the hydrazin group, in which the phenyl members are distributed symmetrically among the two nitro-groups.

The author adduces several reactions of each of these isomeric compounds to confirm the above view, the most important of which is, that on dry distillation the diphenyl-hydrazin yields diphenylamine and ammonia, whereas the hydrazobenzene yields aniline and azobenzene. Their behaviour with nitrous acid, however, does not yield much in support of this view, for while the hydrazobenzene yields a body bearing great resemblance to the ordinary nitroamines, the diphenylhydrazin yields nitrous oxide and diphenylnitrosamine, which

reaction may be explained in several ways. But the author inclines to the view expressed in the formula—



the nascent diphenylamine reacting with another molecule of HNO_2 , forms the nitrosamine. He is the more inclined to support this view, as no other means of oxidation than nitrous acid is effectual.

Should the same reaction hold good with the remaining unsymmetrical secondary hydrazins (which has not yet been proved), nitrous acid might prove a valuable reagent in distinguishing between these bases: the primary yielding easily decomposable nitro-derivatives, passing on dehydration into the compounds corresponding with diazobenzylamide, while the secondary would either be reconverted into the corresponding nitrosamines, or into nitro-derivatives richer in nitrogen. The same may be expected of the tertiary bases; but the quaternary will either remain unacted on, or will yield bodies analogous in constitution to the nitrosodimethylaniline discovered by Baeyer and Caro.

C. L. F.

Preparation and Estimation of the Amine-bases by the formation of their Alums. By W. KIRCHMANN. (*Arch. Pharm.* [3], x, 43—44).—This method, which the author has employed for detecting the presence of amine-bases in the fruits of the *Heracleum asperum*, consists in exhausting the raw material at 100° with carbonic acid, and fixing the amines in the form of beautifully crystallised alums. 60 grams of the dried fruits were pressed and moistened with an excess of soda-lye; they were then boiled and extracted with carbonic acid. The latter dissolved ethereal oils and an amine-base, which it gave up to water acidulated with sulphuric acid, retaining the ethereal oil. The acid solution of the amine sulphate was supersaturated with alumina, filtered and evaporated, when 2—3 grams of an alum were obtained, the alkali of which was replaced by an amine-base. The alum-compound was dissolved in water, and soda-lye added in order to take up the alumina, while the pure base was extracted by chloroform. It formed on evaporation a liquid smelling like conine and difficultly crystallisable. Its chlorine-compound crystallised in needles, but deliquesced very quickly. The base did not give the characteristic smell of the carbamines when treated with chloroform and an alcoholic solution of caustic soda, thus proving that the *Heracleum*-base is not a monamine.

Fruct. anethi graveolentis, when treated in the same manner, also gave a large quantity of an amine-alum.

D. B.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXI.—*On the Coal-gas of the Metropolis.*

By T. S. HUMPHDRE, Jodrell Scholar.

AN accurate knowledge of the constituents of the coal-gas supplied to the Metropolis is of some scientific interest and much public importance; nevertheless, few complete analyses of the Metropolitan gas have been published. I am not acquainted with any complete analytical examination of the gas consumed in the Metropolis since the year 1851, when Dr. Frankland collected samples of the gas delivered by all the London companies, and made complete analyses of them.

I trust, therefore, that the following results of recent analytical and photometric observations, which I have now the honour to lay before the Chemical Society, will not be altogether unacceptable.

These results, when compared with those of Dr. Frankland, show (i) that the gas now delivered in London is no better than that supplied 25 years ago; (ii) that the increase in the illuminating power announced from the various testing-stations is to be attributed to improvements in the test-burner, and not to any intrinsic augmentation in the illuminating power of the gas.

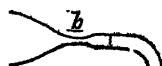
The samples of gas I have examined were collected from—

- (i.) The Royal College of Chemistry, South Kensington, S.W.
- (ii.) The City Gas Examiner's Office, 8, Savage Gardens, E.C.
- (iii.) The Testing House, Beckton.
- (iv.) Crane-grove, Holloway-road, N.W.
- (v.) The Engineer's Office, Houses of Parliament.

They were all carefully collected in sealed tubes, the air of which was displaced by a rapid current of the gas. The method of collection was as follows:—

A piece of soft glass tubing, drawn out at the ends, about 5 inches long and an inch in diameter, was connected at one end with the supply of gas, and from the other end a long piece of caoutchouc tubing was allowed to hang.

The tube being placed horizontally, the gas was passed until all air was expelled, after which the current was stopped and the tube sealed with a blowpipe, first at *a* and then at *b*.



The apparatus employed for the analysis of the gases was that modification of Messrs. Frankland and Ward's, described by Professor Macleod, in the Journal of this Society, vol. xxii, p. 313. The determinations could be made with great rapidity, three hours being sufficient for a complete analysis.

The percentages of the following gases were determined:—Carbonic anhydride, oxygen, nitrogen, hydrogen, marsh-gas, carbonic oxide, and the hydrocarbons absorbed by fuming sulphuric acid; and the mode of analysis was that described in Bunsen's Gasometry, and the chapter on gas analysis in Sutton's Volumetric Analysis.

With regard to the gases absorbed by fuming sulphuric acid, their carbon-density (or value of n in the formula C_nH_m) was determined, as well as their percentage volume. This carbon-density is obviously expressed by the volume of carbonic anhydride produced by the combustion of one volume of the hydrocarbons, thus:—



and this CO_2 was found in the following manner:—

The heavy hydrocarbons in 100 volumes of the gas were first removed, and then the volume of carbonic anhydride produced by the combustion of the residue determined. Call this A. Then the volume of carbonic anhydride produced by the combustion of 100 volumes of the entire gas was determined, and called B. Now, if the percentage of the condensable hydrocarbons be represented by C, the volume of carbonic anhydride produced by the combustion of one volume of these gases, in other words, their carbon density, or the value of n in the formula C_nH_m will be:—

$$\frac{B - A}{C}$$

Again, their equivalent in olefiant gas (*i.e.*, where $n = 2$), for

100 volumes of the gas, is found by multiplying their percentage by half their carbon-density, *i.e.*—

$$\frac{C d}{2}$$

(where *d* = density),

or substituting the value of *d* obtained above,

$$\frac{B - A}{2}.$$

Dr. Frankland has shown (*Chem. Soc. Jour.*, vol. v, p. 39), that marsh-gas and carbonic oxide are as much without illuminating power as hydrogen, and therefore that the illuminating power of a gas is quite independent of these constituents.

In the case of *cannel* gases, the illuminating power can be calculated from the equivalent of olefiant gas; but in *coal* gases, traces of other hydrocarbons are present, possibly paraffins,* which are incon- densable by fuming sulphuric acid. They influence the illuminating power, however, to a scarcely perceptible extent.

Berthelot (*Compt. rend.*, lxxxii, 871) has recently stated that the coal-gas of Paris owes nearly the whole of its illuminating power to the vapours of benzene, but as the vapour of benzene is absorbed by fuming sulphuric acid, this circumstance does not affect the analytical results given below. These results, moreover, show that the London gases contain considerable quantities of other illuminating hydrocarbons absorbable by sulphuric anhydride, for the carbon-density of benzene vapour is 6, whereas that of the absorbable hydrocarbons in the London gases never exceeds 4·5, and averages only 3·6.

In nearly all cases, several analyses of each sample of gas were made, and as a proof of the accuracy of the method, I append the following pair of results:—

Houses of Parliament (Cannel Gas).

		CO ₂ .	O.	H.	CO.	CH ₄ .	N.	Heavy hydrocarbons absorbed by SO ₂ .
(i)	..	None ..	None ..	41·46	4·63	42·24	2·75	8·92
(ii)	..	None ..	None ..	41·72	4·98	41·88	2·71	8·72

From two places, *viz.*, the City Gas Examiner's Office and the College of Chemistry, samples of gas were taken in the daytime and evening of the same day. The results of these analyses are given below, with those of the other samples.

* These paraffins are said to be ethylic, propylic, and butylic hydride, particularly the two latter (*Chem. Soc. Jour.*, iii, 42).

TABLE I.—*Dr. Frankland's Determinations, July, 1851.*

		CO ₂	O.	N.	H.	CO.	CH ₄	C ₂ H ₆	Carbon-density.	Equivalent in C ₂ H ₄
1.	<i>City Co.</i> , taken at Blackfriars (Newcastle Coal).	0·53	47·60	7·32	41·50	3·06	4·57	6·97
2.	<i>Great Central Co.</i> , taken at office, Coleman-street, 3 miles from works (Newcastle Coal and Cannel).	0·28	0·44	1·80	51·24	7·40	35·28	3·56	4·06	7·21
3.	<i>Western Co.</i> , taken at works, Paddington (Newcastle Cannel).	0·13	0·48	1·51	25·32	7·85	51·20	13·06	3·52	22·98
4.	<i>Imperial</i> , taken ½ mile from Battle Bridge Works.	0·29	1·20	5·01	41·15	8·02	40·66	3·67	3·35	6·15
5.	<i>Chartered</i> , taken ¼ mile from works, Brick Lane.	None.	0·08	0·38	51·81	8·95	35·25	3·53	4·36	7·70

TABLE II.—*Determinations, May, 1876.*

		CO ₂	O.	N.	H.	CO.	CH ₄	C ₂ H ₆	Carbon-density.	Equivalent in C ₂ H ₄
1.	<i>Imperial Co.</i> , Crane Grove, Holloway Road 10.30 p.m.	None.	1·91	9·73	40·32	6·79	36·57	4·18	3·81	7·96
2.	<i>Chartered Co.</i> , .. noon	None.	Traces.	3·48	50·59	3·13	38·39	4·41	3·56	7·85
3.	<i>Beckton Testing House</i> noon	None.	0·22	4·98	50·28	4·37	36·95	3·22	3·94	6·34
4.	<i>Chartered Co.</i> , Mr. Heisch's office .. 11.30 a.m.	None.	0·60	3·22	50·62	6·96	34·49	4·11	3·16	6·49
5.	<i>Chartered Co.</i> , Mr. Heisch's office .. 9.30 p.m.	Traces.	0·26	4·93	50·68	3·98	35·89	4·08	3·26	6·65
6.	<i>Royal College Chemistry</i> .. noon	Traces.	0·40	5·40	43·99	6·42	39·36	4·12	3·31	6·82
7.	<i>Royal College Chemistry Houses of Parliament, (Cannel)</i> 7 p.m.	None.	None.	2·71	41·72	4·98	41·88	3·72	4·51	19·66

By comparing these analyses made at an interval of 25 years, it is clearly seen that the real illuminating power has not increased, and that in the case of cannel gas it has actually decreased.

On examining the results obtained from different burners, it is found that the supposed improvement is due to the *burner and not to the gas*, as is seen from the following comparative photometric experiments which were all made at the Royal College of Chemistry with the usual Bunsen photometer. Each number is the mean of ten observations.

The gas was always burnt uniformly at the rate of 5 cubic feet per hour, and the candle reduced to 120 grains of sperm per hour.

TABLE III.—*Results of Photometric Experiments.*

Burner.	June 6th, 4 p.m.		June 28th, 3 p.m.	
	Pressure.*	Candles.	Pressure.*	Candles.
Silber's "G" Burner	$\frac{2}{1\frac{1}{2}}$	14.6 (α)	$\frac{2}{1\frac{1}{2}}$	16.6 (β)
Present Referee's Test-burner	$\frac{2}{1\frac{1}{2}}$	14.3	$\frac{2}{1\frac{1}{2}}$	14.5
Test-burner used from 1860 to 1866 ..	$\frac{2}{1\frac{1}{2}}$	13.1	$\frac{2}{1\frac{1}{2}}$	12.5
Test-burner used previous to 1860	$\frac{2}{1\frac{1}{2}}$	11.1	$\frac{2}{1\frac{1}{2}}$	10.5

We see from these numbers that a gas which, tested by the burner used for that purpose previous to 1860, gave an illuminating power of only 10.5 candles, afforded with the present test-burner a light of 14.5 candles.

Silber's Argand burners, yielding the results α and β , were marked respectively G 1,556 and G 6,671; α had 40 holes, whilst β had 25 holes. It is thus evident that a gas which gives, in the burners almost universally employed by consumers, a light equal to only 10.5 candles, registers when burnt in G 6,671, a light equal to 16.6 candles.

In conclusion, I have to express my thanks to Dr. Frankland for his help throughout this investigation, and I append the following table, for which I am indebted to Mr. A. Vernon Harcourt, F.R.S., showing that during the month in which my experiments were made, the illuminating power of the gas delivered by the Chartered Gas Light and Coke Company never fell below the Parliamentary standard of 16 candles for a consumption of 5 cb.c. feet per hour, *when it was tested during the prescribed hours, and with the so-called Referee's burner.*

In other words, the Company was strictly complying with the Act of Parliament.

* In inches of water, between the regulating cock and the burner.

Date, 1876.		Gas Light and Coke Company.							South Metropolitan Gas Company.	
		Beckton.	Bow.	Millbank.	Kensal Green.	Bromley.	Fulham.	St. Pancras.	Dalston.	Peckham.
May 1 ..	—	—	—	—	—	—	—	—	—	No report of testings received.
" 2 ..	16·9	16·5	21·2	16·7	—	—	—	—	—	
" 3 ..	16·8	16·2	20·5	16·5	16·7	16·7	17·1	16·6	16·7	No report of testings received.
" 4 ..	17·6	16·0	20·7	16·8	16·8	16·8	—	17·3	17·4	
" 5 ..	17·1	16·2	21·0	16·5	16·7	16·7	No report of testings received.	15·8	17·2	
" 6 ..	17·4	16·1	21·1	16·5	16·2	16·5		16·0	18·0	
" 7 ..	17·2	16·3	20·7	16·3	16·5	16·5	16·3	17·0	16·8	
" 8 ..	16·6	16·5	..	16·6	16·8	16·8	16·7	17·7	16·8	
" 9 ..	17·2	16·4	20·5	16·8	16·6	16·6	17·0	17·5	17·5	
" 10 ..	17·1	16·6	21·2	16·7	16·1	16·4	17·1	17·2	16·4	
" 11 ..	17·0	16·5	21·0	16·7	15·8	16·8	17·3	16·8	16·8	
" 12 ..	17·1	16·9	20·5	16·2	16·2	16·8	16·8	17·3	16·8	
" 13 ..	17·7	16·1	20·4	16·9	16·7	16·7	17·1	17·1	17·5	
" 14 ..	18·0	16·3	..	16·5	16·4	16·6	16·5	16·2	17·6	
" 15 ..	17·3	16·5	21·7	17·4	16·6	17·1	16·7	16·7	17·4	
" 16 ..	17·2	16·3	20·5	16·7	16·9	16·9	16·8	17·8	17·5	
" 17 ..	18·0	16·4	20·8	16·7	16·5	16·8	16·7	17·5	15·6	
" 18 ..	18·3	16·8	20·8	17·2	16·5	16·8	16·6	17·8	16·6	
" 19 ..	17·2	16·8	21·2	16·9	16·8	16·8	16·5	17·7	16·3	
" 20 ..	16·8	16·7	22·2	16·6	16·4	16·4	16·5	17·5	—	
" 21 ..	16·8	16·7	..	16·6	16·5	16·7	16·6	17·1	—	
" 22 ..	16·8	16·7	..	16·1	16·7	16·7	16·6	17·0	—	
" 23 ..	16·8	16·3	..	16·6	16·8	16·8	16·8	17·3	15·1	
" 24 ..	17·5	16·4	21·0	16·7	16·8	16·8	17·0	17·0	15·4	
" 25 ..	17·4	16·1	20·5	17·0	17·1	17·1	16·7	17·8	15·1	
" 26 ..	17·8	16·1	21·2	16·6	17·0	17·0	16·7	17·9	15·5	
Average.....	17·24	16·4	20·935	16·7	16·57	16·8	16·75	17·25		

XXII.—*On the Theory of the Bunsen Lamp.*

By T. E. THORPE, Ph.D., F.R.S., Professor of Chemistry in the
Yorkshire College of Science, Leeds.

(A Lecture delivered before the Chemical Society, March 1st, 1877.)

It is hardly necessary in an assembly of chemists to extol the merits or the services of the Bunsen lamp: it may be safely asserted that no single piece of our apparatus has done more to facilitate our labour or to increase our productiveness. We can only realise how intimately associated it is with our comfort as workers, when we endeavour to imagine to what we should be driven if we were deprived of it.

And it is not only to the scientific man that this instrument is of service; there are many trades to which it has become as indispensable as it is to us. But in spite of this very general application, it is only quite recently that we have obtained clear notions of its action. To this end, the labours of Bunsen himself have contributed, directly and indirectly, in the greatest degree; for his studies in connection with the general properties of gases not only led him, in the first place, to the recognition of the principles upon which the lamp is constructed, but they have served, in the second, owing to the precision which he gave to gasometric analysis, to clear up much of what has hitherto been obscure in its theory.

During the past four or five years a number of investigators have studied the phenomena presented by the Bunsen flame, more particularly in relation to the general question of the theory of luminous flames, and thanks to the observations of Blochmann, Heumann, Knapp, and others, it is now possible to offer a tolerably complete account of the theory of its action. I have thought, therefore, that a brief statement of what appears to be the present state of knowledge upon a subject of no little concern to us all as chemists, might not be without interest to the Fellows of this Society.

The story of the origin of the lamp may be told in a very few words. Bunsen, when planning the fittings of his present laboratory, had arranged for the introduction into it of coal-gas as a fuel. An eminent Fellow of this Society—Professor Roscoe—had brought under his notice some of the contrivances which were then in use in this country for burning coal-gas with a smokeless flame. There are doubtless many here who can well remember these pieces of apparatus: possibly to some they are associated with the memories of disasters ending in the loss of much glass and precious material and still more precious time: these at least will not be surprised to learn

that our distinguished foreign member pronounced them as unworthy of the fuel they had to burn. Bunsen's inventive power was in immediate exercise, and no very long time elapsed before Universitäts-Mechanikus Desaga was able to put his ideas into brass and iron.

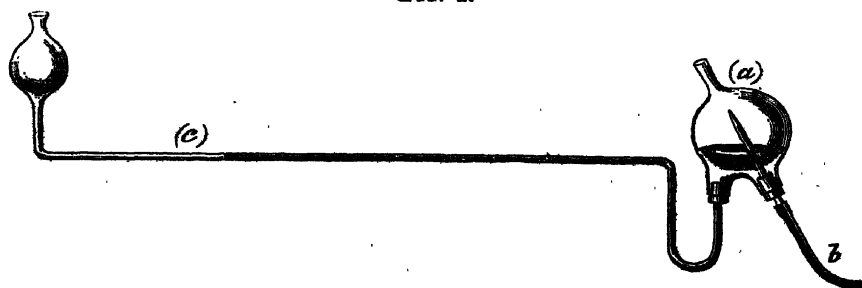
Of course it is hardly to be supposed that the lamp at once took the form and proportions of the instrument with which we are all familiar, but, as you will see from this drawing which Mr. Desaga has been so good as to prepare for me, the first lamp differed but slightly from those now used, the main alteration being in the height and width of the tube.

It is unnecessary for me to trouble you with any details of the construction of the present form of lamp. You know that essentially it consists of a brass tube, at the bottom of which is a small opening for the entrance of coal-gas; in the tube and close to the jet are holes through which air passes and mixes with the up-streaming gas, in such proportions that the mixture burns at the mouth with a non-luminous flame. That the air is actually concerned in the destruction of the luminosity of the flame, is evident from the circumstance that by closing the holes in the tube either with the fingers or with the movable regulator which is now commonly attached to the lamp, the flame again becomes luminous. You are also doubtless aware that in order that the flame may not retreat down the tube, it is necessary that a certain relation shall exist between the height and width of the tube, the area of the air-holes, and the amount and velocity of the issuing gas. There are other conditions which determine the proper behaviour of the burning lamp, which we shall have an opportunity of discussing hereafter.

And first, then (to begin at the beginning), let us consider the mode by which the air is caused to mix with the inflammable gas. How is it that by piercing the tube close to the burner with holes sufficiently wide, air flows in and mixes with the gas in such proportions as to give a non-luminous flame? There is a well-known experiment, first made by Clement and Desormes, and mentioned in most text-books of physics, which serves to illustrate the cause. These physicists found that when a small opening was made in a box containing compressed air, and a disc of wood or metal was held against the stream of issuing gas, the disc was forcibly driven towards the hole in the reservoir; that is, against the out-rushing air; the disc oscillated backwards and forwards in the air-stream within a short distance from the orifice, and required considerable force to drag it away. Faraday was accustomed to show this remarkable and somewhat paradoxical phenomenon in a characteristically simple manner. Placing the fingers of his outstretched hand together, and holding it horizontally, he blew with some

force through the interspace below the knuckles of the first two fingers upon a light card of two or three inches square placed immediately beneath: the card was lifted up and remained suspended, apparently against the action of gravity and the issuing air, so long as the blast continued. These effects are due to the existence of what the meteorologists call an area of low pressure in the neighbourhood of the orifice through which the gas rushes: the issuing stream carries with it more or less of the circumjacent air, partly as the result of its expansion and partly as the result of its viscosity, exactly as the falling water in the trompe of the Catalan forge carries down the air. The simple arrangement which you see on the table (Fig. 1), which is constructed on the principle of the multiplying manometer of Dr. List, which some of you may have seen exhibited in the Loan Collection of Scientific Apparatus, may serve to demonstrate the existence of this area of low pressure in the neighbourhood of a jet through which air rushes. It consists of a small but wide vessel (*a*) connected with a long narrow horizontal tube (*c*) partially filled with coloured spirit; as you

FIG. 1.

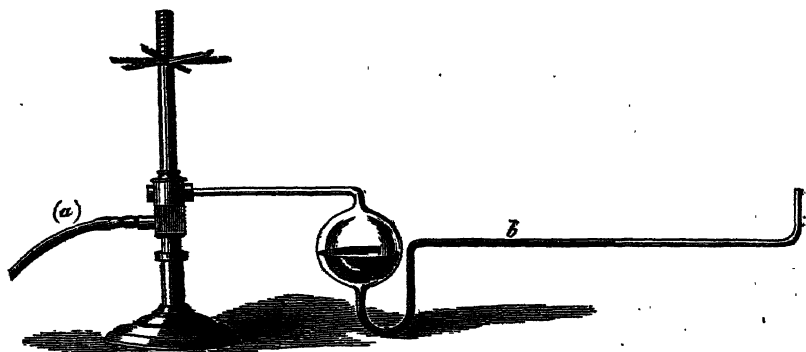


perceive, a very slight increase in the height of the level of the liquid in the wide vessel causes a very considerable column of the coloured liquid to flow out of the horizontal tube. If the diameter of the wide vessel at the surface of the coloured liquid be ten times that of the horizontal tube, a diminution of pressure in the wide vessel capable of raising the spirit 1 cm. high, will cause a displacement of 100 cm. in the column in the horizontal tube. You see that, when I blow into the wide vessel through the narrow glass-tube (*b*) ending above the surface of the liquid, there is an immediate flow of the coloured spirit out of the horizontal tube into the large bulb.

By means of a smaller apparatus constructed on the same principle, I think I shall be able to show you the existence of this rarefaction in the neighbourhood of the burner of the Bunsen-lamp as the gas issues through it, despite the low pressure with which it is driven into the air. One of the air-holes of this lamp (Fig. 2) is closed with a cork,

the other is connected with a little manometer (*b*) : you see, as I turn on the gas, the liquid in the narrow horizontal tube immediately flows into the wide bulb.

FIG. 2.



The intermixture of the gas and the air thus driven in is greatly facilitated by the rapid spreading out of the gas stream after leaving the burner. If you substitute a glass-tube for the ordinary brass tube of the lamp, and cause the gas to burn at the bottom, you will notice from the shape which the flame assumes in the first few moments, that the gas at a height of a very few millimeters above the burner flows out in a curve towards the walls of the tube as its velocity of efflux diminishes. The flame strikes against the sides of the tube, which rapidly becomes hot, as some of us possibly know to our cost. The amount of air which thus mixes with a given volume of gas varies with the diameter and height of the tube and the area of the air-holes. In the lamp ordinarily used in laboratories, the gas becomes mixed with from 2 to $2\frac{1}{2}$ times its volume of air: this is considerably less than half the amount required for complete combustion. Such a lamp giving a flame of about the average size, that is about 120 mm. in height, burns about 80 litres of gas under $\frac{1}{2}$ -inch pressure in an hour. Hence you see that as much as 250 litres of mixed gases are driven up the tube of each small lamp in a laboratory in the course of an hour.

In certain modifications of the Bunsen-lamp, as in the burner of Mr. Wallace, the proportion of air to gas is greatly increased: in one of the forms devised by him the gas is mixed with as much as $4\frac{1}{2}$ times its volume of air. Such a mixture is within the limits of inflammability; for ordinary gas will not burn when mixed with more than 8 or $8\frac{1}{2}$ times its volume of air, or with less than 3 volumes, at least at ordinary temperatures. Hence it is only by the special contrivance of

a perforated cap that the flame is prevented from retreating down the wide tube.

This leads us to the consideration of another point connected with the theory of the lamp, which may become of paramount importance under certain conditions. You know that it is possible to burn a mixture of one volume of oxygen and two volumes of hydrogen, at the end of a narrow tube without exploding the mixture in the reservoir, provided that the explosive mixture is driven with sufficient rapidity through the tube. If the velocity of efflux of the mixed gases is greater than the rate of propagation of inflammation from particle to particle, there is no risk of exploding the detonating mixture in the reservoir; if, however, the pressure on the mixed gases is diminished so that the rapidity of inflammation becomes greater than that of the efflux of the gases, the flame passes along the tube into the reservoir, and an explosion results. The rapidity of inflammation of a gaseous mixture depends mainly upon two factors: (1) the temperature of inflammation, that is, the temperature required to initiate the chemical union; and (2) the temperature of combustion, that is, the temperature produced by the chemical union. The rapidity of inflammation of a mixture of detonating gas and of carbon monoxide and oxygen, has been determined by Bunsen, by observing the velocity with which the mixed gases must travel through a small aperture in order that the position of the flame may be maintained constant. He thus found that the rate of propagation of combustion in the mixture of oxygen and hydrogen was 34 meters in a second of time, whereas in that of the carbon monoxide and oxygen it was less than 1 meter per second. He also found, as indeed we should expect from the conditions which determine the rapidity of inflammation, that an excess of one or other constituent, or an admixture of an indifferent gas rapidly diminished the rate. Bunsen also observed that a mixture which was explosive in the open air could be fired in a closed vessel, as in this case no heat is absorbed by the free expansion of the gas.

We have to thank Professor Mallard, of the French School of Mines, for a series of observations made by Bunsen's method, on the rate of propagation of combustion in mixtures of coal-gas and air, and of marsh-gas and air, undertaken in view of the relation of the question to the theory of safety-lamps (Mallard, *Annales des Mines*, vol. vii, 1875, p. 355). Although we are more immediately concerned with the matter as affecting the special case of coal-gas, it may not be uninteresting to state that, in mixtures of fire-damp and air, the maximum rapidity of inflammation was found to be about 0.56 m. or rather more than $\frac{1}{2}$ yard per second; this corresponded to a mixture of 1 vol. of marsh-gas and $8\frac{1}{4}$ vols. of air. When the proportion of air was

increased to 12 vols. or diminished to 5.9 vols., the mixture was neither explosive nor inflammable. It is worthy of note that the proportion of air corresponding to the maximum rate of inflammation is less than that which contains the oxygen necessary for the complete combustion of the marsh-gas.

The maximum rapidity of the propagation of combustion in mixtures of coal-gas and air is much greater than in the case of fire-damp and air, as indeed we should be led to anticipate from the large quantity of free hydrogen which coal-gas invariably contains. The maximum rapidity of the particular sample of coal-gas examined by M. Mallard was 1.02 m. or rather more than 1 yard per second: this occurred in a mixture of 5 vols. of air and 1 vol. of gas. As in the case of other gases, the rate is very rapidly diminished by an excess of either constituent; a mixture containing more than 8 vols. and less than $3\frac{1}{2}$ vols. of air to 1 of coal-gas was found to be uninflammable.

The results of M. Mallard's observations are contained in Table I.

TABLE I.

Vols. of air mixed with 1 vol. of coal-gas.	Rapidity of inflammation in meters per second.
$6\frac{1}{2}$	0.285
6	0.617
$5\frac{1}{2}$	0.820
$5\frac{1}{4}$	0.985
5	1.010
$4\frac{3}{4}$	0.935
$4\frac{1}{8}$	0.740
$3\frac{1}{2}$	0.097

The bearing of these observations on the theory of the Bunsen lamp will be at once evident to you. We notice that we could burn even the most inflammable of the mixtures at the top of the tube, provided that we could maintain the ascending column at a greater velocity than 1.02 meters per second. As we have said, the gas passing up the tube of the ordinary lamp in the case of a flame about 120 mm. high is mixed with from 2 to $2\frac{1}{2}$ times its volume of air: if the proportion of air rises to $3\frac{1}{2}$ vols., the mixture would have to arrive at the opening of the tube with a velocity greater than 0.097 meter per second, otherwise the flame would retreat. Of course, in practice a greater initial movement than this would be required in order to provide against loss of motion due to friction against the sides of the tube, in consequence of which the centre of the gas stream always moves faster than the outlying portions. This retardation, which may be considerable in dirty or corroded tubes, frequently induces

the flame to retreat: the main body of the inflammable stream may be moving with the velocity necessary to prevent retardation, whilst the sluggish outer layers are powerless to oppose it. Any arrangement which ensures that the minimum velocity of efflux of the mixture is greater than the rate of propagation of combustion, will prevent the retreat of the flame, but the most obvious course, that of increasing the gas pressure, is not always possible. In cases where the gas pressure is invariably low, perhaps the simplest method is to turn in the upper end of the tube, as proposed by Professor Morton, or what comes to the same thing, to lay a small perforated disc on the top of the tube. The rate of movement of the various portions of the gas-stream is thus equalised. The rose which is commonly attached to the lamp, the perforated cap of Mr. Wallace's burner, or the little bit of wire-gauze which we place on the top of the tube when we desire a very small flame, owe their efficacy partly to the same action, and partly to their cooling effect on the flame.

Having thus traced the progress of the mixture of air and gas up the tube, let us now turn our attention to the flame itself. In the first place, we notice that it is hollow; that is, it contains a large internal area consisting of the uninflamed mixture: the issuing stream in which the gas is mixed with only about twice its volume of air, is, as we have seen, uninflamable: it is only, therefore, at the margin where the requisite additional amount of oxygen is met with, that combustion occurs. The existence of this internal area of unburnt and comparatively cool gas may be demonstrated by the simple experiment of supporting a lucifer match down the tube by means of a pin pushed transversely through the splint, so that the head of the match appears a few millimeters above the mouth of the tube. On lighting the lamp, the flame appears to envelop the match, which, however, is not ignited. A piece of gun-cotton placed in the same position is not inflamed. It must not be supposed, however, that the composition of the mixture is the same in all parts of the internal area, for the products of the combustion of the marginal portions find their way into the stream of unignited gas.

We are indebted to Dr. Blochmann for a series of observations on this and many other points connected with the Bunsen lamp (Blochmann, *Ann. der Chem. u. Pharm.*, 168, 295). By methods similar to those already adopted by Landolt and Hilgard in the case of luminous flames, he has traced the gradual alteration in the composition of the mixture at different points in the internal area, viz., at 25 mm. and 50 mm. above the opening of the tube, and he has also determined the nature of the gases in the flame itself at a distance of 75 mm. from the tube. The flame studied by him was 120 mm. high, and the point of the inner zone varied from 55 to 60 mm. from

the end of the tube. The coal-gas, which varied but slightly in composition in the course of the observations, issued under a pressure of 12 mm., and was mixed with air in the tube in the proportion of 28·26 vols. of gas to 71·74 vols. of air, or slightly more than $2\frac{1}{2}$ vols. of air to 1 of gas. The percentage composition of the gases drawn from the various points is given in Table II.

TABLE II.

	Mixture in the tube 10 mm. below the opening.	25 mm.	50 mm.	75 mm.
H	13·74	9·68	4·84	2·80
CH ₄	11·02	10·78	7·64	0·99
CO	0·80	0·58	2·99	2·21
C ₂ H ₄	1·13	0·90	0·60	—
C ₂ H ₆	0·85	0·66	0·44	—
O	14·88	13·85	5·92	—
N	56·47	59·58	61·66	66·55
CO ₂	0·21	0·93	3·55	7·25
H ₂ O	0·90	3·14	13·66	20·20

On comparing the composition of the gases in the tube with that of the mixture in the middle of the internal area, we see that the only important difference is that a certain amount of the free hydrogen, of which the ignition-point is comparatively low and the rapidity of inflammation very high, has been consumed: the effect of this we see in the increased proportion of water-vapour. We also notice, from the increased amount of nitrogen, and from the fact that the quantity of oxygen is sensibly the same as in the mixture in the tube, that an additional amount of air has been mixed with the gas. At a height of 50 mm., the effect of this admixture of combustion-products with unburnt gas is more marked, and we see that the proportions of water-vapour and oxides of carbon are greatly augmented.

Table III represents the proportion of air which has mixed with 100 vols. of the coal-gas at the different points, and shows, even more clearly, the nature of the changes in the composition of the mixture at the various stages of its flow and combustion.

TABLE III.

Amount of air mixed with 100 vols. of gas.	In the tube.	25 mm.	50 mm.	75 mm.	Complete combustion.
	253·9	284·7	284·5	484·3	608·8
H	48·6	36·4	17·7	16·1	—
CH ₄	39·0	40·1	28·0	5·7	—
CO	2·9	2·2	19·9	12·7	—
C ₂ H ₄	4·0	3·4	2·2	—	—
C ₄ H ₈	8·0	2·5	1·6	—	—
O	52·7	52·0	21·7	—	—
N	199·8	223·8	225·9	382·4	482·3
CO ₂	0·8	3·5	13·0	41·7	62·4
H ₂ O	3·1	11·8	45·8	116·1	141·2
	353·9	375·7	369·8	574·7	685·9
Contraction	9·0	14·7	10·1	22·9

This table also shows us that of the two combustible gases of which coal-gas is chiefly composed, namely, marsh-gas and hydrogen, the hydrogen is the first to burn: we see the effect of this in its diminished proportion in the gases at 25 mm. and 50 mm. above the tube. The cause of this rapid diminution in the proportion of the hydrogen is to be ascribed mainly to the greater diffusive power of that gas, to its lower ignition-point and to its greater rapidity of inflammation as compared with marsh-gas. It is known that a red-hot wire causes the combination of a mixture of oxygen and hydrogen, whereas it has no effect on a mixture of marsh-gas and oxygen. That this rate of diminution in the proportion of the hydrogen can be maintained is hardly to be expected; for in the partition of the oxygen between the two combustible gases, we soon arrive at a condition of things analogous to that observed by Bunsen in the case of the combination of a mixture of carbon monoxide and hydrogen with oxygen gas. The rate of the combustion of the hydrogen very rapidly diminishes as its proportion decreases, and that of the marsh-gas increases. At a height of 75 mm., that is, at about one-third of the distance between the top of the inner zone and the visible limit of the flame, the amount of the marsh-gas is only about one-third of that of the hydrogen. The increased ratio of the hydrogen is probably due to the high temperature of this part of the flame: the temperature of combustion of the marsh-gas in air is high enough to prevent the complete combustion of the hydrogen, or, what comes to the same thing, is sufficiently high to dissociate vapour of water already formed. The large proportion of carbon monoxide present in the neighbour-

hood of the summit of the inner cone accords with our every-day experience of the reducing action of this portion of the flame.

We see from Table III, that in the combustion of coal-gas a considerable contraction of volume occurs: 708·8 vols. of air and gas give only 685·9 vols. of combustion-products. On the whole, the rate of the contraction goes on increasing with the height of the flame, but you notice that at 75 mm. a sudden break in the continuity of the rate is manifest. This is owing to an increase in the volume of the still unburnt gas due to the decomposition and partial oxidation of the hydrocarbons: *e.g.*, 1 vol. of ethene with 1 vol. of O, gives 2 vols. of carbon monoxide and 2 vols. of free hydrogen.

Blochmann has also analysed the gases present in the extreme outer edge of the flame: these, of course, consist of water-vapour and carbonic acid mixed with oxygen and nitrogen.

The results are contained in the following table:—

TABLE IV.

Height from burner, mm.	CO ₂ .	H ₂ O.	O.	N.	$\frac{\text{H}_2\text{O.}}{\text{CO}_2}$.
10	3·30	14·36	8·29	74·05	4·35
20	3·49	14·95	7·95	73·61	4·29
30	4·07	14·68	8·31	72·94	3·63
40	3·95	12·90	8·94	74·21	3·27
50	3·64	11·22	10·03	75·11	3·08
60	3·92	11·02	9·72	75·34	2·81
70	4·35	10·82	9·20	75·63	2·49
80	4·91	10·73	8·92	75·44	2·18
90	5·38	10·72	8·60	75·30	1·99
100	5·73	10·81	7·76	75·70	1·89
110	6·58	10·97	6·61	75·84	1·67
120	7·18	11·14	6·17	75·51	1·55

These numbers also serve to indicate what we have before noticed, *viz.*, that the greater portion of the hydrogen present in the coal-gas is consumed in the lower parts of the flame. We observe that the greatest proportion of the water-vapour is formed in the lowest quarter of the flame; it then gradually decreases up to a height of about 90 mm., after which it slowly increases. This corresponds exactly with what we noticed in connection with the composition of the gases in the interior of the flame. On the other hand, the proportion of carbon dioxide suffers a pretty steady increase with the height of the flame, as we should expect. It should be noted, however, that the whole of the water and carbon dioxide drawn through the tube at the particular heights above given, cannot be considered

as having been actually formed at those points, since there is no doubt that a certain amount of these gases must have diffused into those spaces from other regions of the flame.

Blochmann, lastly, has determined the amount of the products of combustion in the atmosphere immediately surrounding the flame, drawn at a distance of 10 mm. from the edge. His results, which are contained in Table V, show that, below a distance of 20 or 25 mm. from the opening of the tube, not a trace of the products can be found: it is only at a height of about 30 mm. that these become perceptible. The ratios in the fourth column afford additional proof of what we have before noticed, viz., that the free hydrogen burns proportionately faster than the hydrocarbons: at a height of 60 mm., and upwards, we find that the ratio of water-vapour and carbon dioxide becomes constant, and almost identical with that given by the complete combustion of the gas, showing, therefore, that the marginal portions of the coal-gas are completely consumed.

TABLE V.

Vertical height from opening of tube.	H ₂ O. Vapour.	CO ₂ .	$\frac{\text{H}_2\text{O.}}{\text{CO}_2}$.
20 mm.	0.06	0.00	—
30	0.77	0.16	4.8
40	1.14	0.40	2.8
50	1.73	0.63	2.7
60	1.90	0.75	2.5
70	2.42	1.05	2.3
80	3.71	1.37	2.7
90	2.40	0.91	2.6
100	2.70	1.10	2.4
110	2.90	1.13	2.6
120	2.74	1.30	2.1
100 vols. of gas give	137.79 vols.	62.62 vols.	2.3

We all know that if we cover the air-holes of the Bunsen-lamp with our fingers, or with the movable cap on the tube, the flame at once becomes luminous; on uncovering the holes, we observe that it immediately resumes its ordinary appearance. What is the cause of this? The usual opinion seems to be that the coal-gas has become mixed with an amount of oxygen, contained in the air drawn in at the base, sufficient to burn any separated carbon to non-luminiferous gases. There is no doubt that even a comparatively small admixture of air destroys the illuminating power of coal-gas. The observations of Silliman and Wurtz (*Sill. Am. J.* [2], xlviii, 40), show that on mixing coal-gas, of ordinary composition, with a-fourth of its

volume of air, its illuminating power is diminished by nearly 85 per cent.: hence it does not seem remarkable that the mixture burning at the mouth of the Bunsen lamp, which contains from 60 to 70 per cent. of air, should give a non-luminous flame. How, then, is the luminosity destroyed? It is easy to show that the oxygen is not necessarily the true cause; indeed, the effect is much more to be attributed to the nitrogen. The Bunsen-lamp before you (Fig. 3)

FIG. 3.

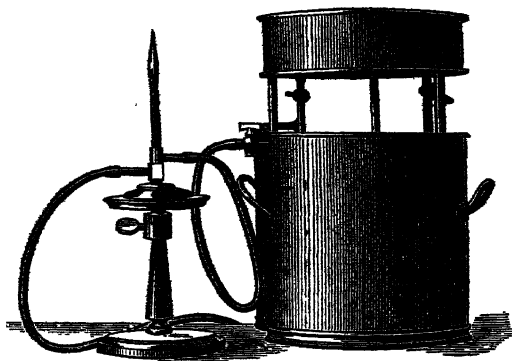
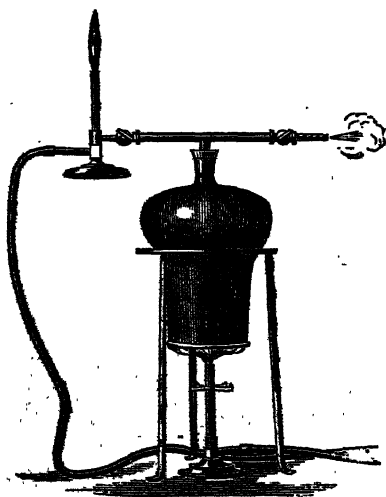


FIG. 4.



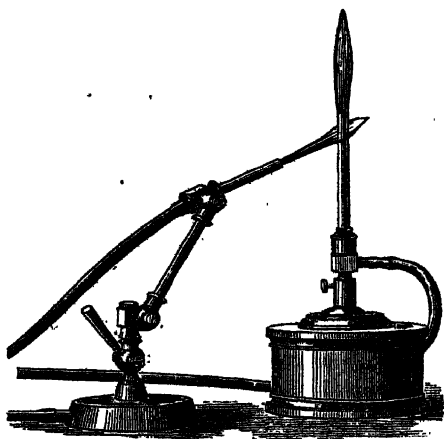
is screwed a small tube connected with a gasholder containing nitrogen; the other hole is closed by the cap: when I allow the nitrogen to pass into the burner and mix with the issuing gas, you notice that the luminosity rapidly diminishes and is eventually destroyed: the flame now acquires an appearance very similar to that of the normal Bunsen-flame. Knapp, to whom we owe this remarkable observation, has shown that any indifferent gas, as carbon dioxide or hydrochloric acid, will produce exactly the same result. Indeed, if I connect the tube inserted into the air-hole with this little boiler from which steam is issuing, I shall be able to destroy the luminosity in the same manner (Fig. 4). The most obvious deduction from these experiments is that the non-luminosity of the Bunsen-lamp is due to the dilution of the coal-gas. This result would seem to afford support to

Dr. Frankland's hypothesis of the cause of luminosity in flames; on the other hand, it may be supposed that the simple extension of the luminiferous material over a sufficiently wide area, whereby it meets with a relatively greater supply of oxygen, is an adequate explanation.

The admixture of a large quantity of an indifferent gas with the coal-gas will, of necessity, influence the temperature of the burning mixture, and such a reduction of temperature must, doubtless, have an effect on the illuminating power of the flame. Many years ago, Dr. Frankland proved that a mixture of marsh-gas and air which, under ordinary circumstances, gave a flame almost destitute of illuminating power, on being previously heated nearly to redness burnt with considerable luminosity; and Wibel has recently shown that the ordinary flame of the Bunsen-lamp becomes luminous when the tube is heated. The lamp before you (Fig. 5) has its brass tube replaced by one of platinum; you notice, as I heat the sides of the tube with a blow-pipe flame, the Bunsen-flame becomes gradually luminous; it now resembles the flame we obtained by cutting off the air-supply at the base. On extinguishing the blow-pipe flame and directing a current of cold air from the bellows on the tube, you observe that the luminosity rapidly diminishes: the flame has now recovered its normal appearance. If we repeat this operation with a burner which, as in a previous experiment, we can feed with nitrogen instead of air, precisely the same result follows.

By a slight modification of this arrangement it can be shown that when either gas is heated singly, the same effect is observed, and Heumann has proved that the phenomenon is not due to a permanent alteration in the composition of the coal-gas by the preliminary heating, nor to a diminished supply of air in consequence of expansion. The conclusion is, in fact, irresistible, that the luminosity of the flame in these experiments is due to the added heat alone. The observations of Wibel and Heumann are instructive in their bearing on the hypothesis that the luminosity of a

FIG. 5.



flame is related to the density of the gases or vapours which compose it: although by heating the mixed gases we diminish their density, we nevertheless increase their luminosity. Dr. Frankland has shown us that hydrogen or carbon monoxide, when burned with oxygen under a pressure of from 15 to 20 atmospheres, yields a luminous flame: would it not appear, in the light of the experiments we have just made, that the luminosity is due as much, if not more, to the heat which, under ordinary circumstances, is lost by the expansion of the gases, as to the density of the gases *per se*? To what then is the small luminosity of the Bunsen flame, as compared with that of the ordinary flame, due? To the diluting action of the gases or to their cooling action? Not to the cooling action solely, for that would imply that the ordinary Bunsen flame has a lower temperature than the luminous flame, which we know is not the case. The feeble luminosity of the Bunsen flame is, in fact, due to a number of causes: we have first, a rapid oxidation of luminiferous material to gases of feeble illuminating power by the oxygen in the admixed air; in the second place, we have the presence of diluting gases, which of themselves reduce the illuminating power; and, thirdly, we have heat withdrawn by the indifferent gases, as nitrogen, and the products of combustion, carbon dioxide, and water. We cannot say that the loss of luminosity is due to any one of these causes acting singly. A flame of mixed coal gas and air has a higher temperature than that of the undiluted coal gas, but it requires a still higher temperature in order that a separation of carbon shall occur. The heat given to the gases by raising the temperature of the tube through which they pass is sufficient, when added to that of the combustion, to make the burning mixture luminous.

We have thus traced the mixture of coal-gas and air up the tube, and we have followed its changes during the process of its conversion into its ultimate products. But as we proceed to lower the flame we may notice something of interest. When the flame is very small it will be seen that it does not immediately rest upon the end of the tube. This fact was first observed by Blochmann. The distance between the flame and tube is ordinarily not very large, but by mixing the coal gas with an inert gas, such as nitrogen, it may be greatly increased. If we repeat the experiment of diluting the coal-gas with nitrogen, you will observe that we can separate the flame and tube by several millimeters. This phenomenon is probably due to two causes; namely, to the cooling action exerted by the tube (for if the tube be heated the space diminishes), and to the fact that the velocity of ignition of the mixture is much less than the rate at which the gas issues. Indeed, the cooling effect of the burner may be partly due to its action in lowering the temperature of the gases, and thus diminishing the velocity of the propagation of ignition.

Every-day experience tells us that when the flame is small, there is great risk that the least draught of air, by interfering with the flow of the gas up the tube, or by mixing with the gas in sufficient amount to create an explosive mixture issuing at a less rate than that of its propagation of combustion, may cause the flame to retreat down the tube and burn at the bottom, with the production of disagreeably-smelling gases arising from imperfect combustion. The nature of the gases thus formed within the tube has been recently studied by Blochmann, whose results are seen in Table VI (*Ann. der Chem. u. Pharm.* 173, 180).

TABLE VI.

Gaseous mixture.

	Before the combustion.	After the combustion.
H	19·91	9·14
OH ₄	14·82	13·49
CO	2·26	4·64
C ₂ H ₂	0·75
C ₂ H ₄	1·57	0·63
C ₄ H ₈	1·20	0·26
N	46·54	46·54
O	12·25	—
CO ₂	0·45	3·02
H ₂ O	1·00	17·33
Contraction	100·00	95·80
	..	4·20

When the flame burns at the bottom, a very much smaller quantity of air passes into the tube; in the case cited, 58·9 vols. of air were mixed with 41·6 vols. of gas. We notice, on comparing the composition of the gas before burning with that remaining after partial combustion, that the proportion of marsh gas is but very slightly diminished, whereas about half the hydrogen has disappeared, and with the decrease of the hydrogen we have a proportionate increase in the amount of water-vapour. We notice, too, a decrease in the amount of the hydrocarbons of the ethene series, and the existence of acetylene derived from their decomposition in the partially burnt gases. We also observe that the amount of carbon monoxide is more than doubled. To the carbon monoxide and acetylene is due the pernicious effect of this partially consumed gas. We notice, too, that all the free oxygen has disappeared, as, indeed, is to be expected; it is easy to demonstrate its non-existence in the gases issuing from the tube by simply holding a lucifer match over the end: you observe that the paste on the match

melts as I hold it in the tube of the lamp down which the flame has retreated, but it is not ignited: on bringing the match into the free air it at once inflames.

XXIII.—*On the Influence exerted by Ammonium Sulphide in preventing the Action of various Solutions on Copper.*

By F. W. SHAW, Student, and THOS. CARNELLEY, D.Sc. (Lond.),
Demonstrator in the Chemical Laboratory of the Owens College.

RECENTLY one of us published a paper on the Action of Water and various Saline Solutions on Copper (*Chem. Soc. J.*, 1876, ii, 1), and in connection with this subject Dr. F. T. Bond suggested that it would be useful to examine the influence of protecting copper from such action by treating its surface with a solution of an alkaline sulphide; for, looking at the extreme insolubility of copper sulphide generally, one would think that it would exercise a high protective power. In consequence of this suggestion we have tried some experiments with a view of ascertaining whether, and to what extent such is really the case. We have throughout used only ammonium sulphide, and the results obtained are given in the present paper.

The following was the method of procedure:—

Pieces of copper-foil, each of which exposed a surface of 1 sq. dec. in all, were cleaned by immersing them for some time in dilute nitric acid (1 to 6), and then thoroughly washing with distilled water. Half of these were then dipped in dilute ammonium sulphide till they were entirely covered by a thin film of copper sulphide; finally they were taken out and well washed with distilled water. These two lots of copper were prepared just before use and kept under water till transferred to the vessels in which the experiments were to be made.

100 c.c. of each of the liquids whose action was to be tried were placed in beakers, and a piece of the prepared copper-foil dropped into each, care being taken that the metal was entirely covered by the liquid during the whole of the exposure; the experiments were then conducted as described in the paper already referred to.

In each series of experiments two sets were carried on simultaneously in exactly the same manner, with the exception that in one set clean copper was exposed, and in the other copper previously treated with ammonium sulphide; in the following tables this is indicated by the terms "clean" and "sulphuretted." Throughout the amount of copper dissolved is represented in milligrams.

A. Action of Distilled Water.

Series I. *Exposed in Beakers at the Ordinary Temperature.*—Table I gives the results obtained under these conditions, from which it is seen that previous washing with ammonium sulphide does not lessen the action of distilled water, but on the contrary increases it:—

TABLE I.

No. of Experiment.	Time of exposure in hours.									Condition of Copper exposed.
	1	2	3	4	6	24	48	72	96	
1.... {	·02	·03	·04	·04	..	·06	·09	·11	·14	Clean.
	·02	·03	·04	·04	..	·10	·11	·12	·24	Sulphuretted.
2.... {	·00	·02	·02	·02	·04	·08	·22	·32	·38	Clean.
	·00	·02	·03	·03	·05	·16	·28	·34	·40	Sulphuretted.
3.... {	..	·03	·03	..	·04	·06	·09	·22	·14	Clean.
	..	·03	·03	..	·04	·08	·11	·25	·18	Sulphuretted.
Mean.... {	·01	·026	·03	·03	·04	·07	·13	·22	·22	Clean.
	·01	·026	·03	·04	·05	·11	·17	·24	·27	Sulphuretted.

Series II. *Exposed in Beakers at a Temperature of (90—100° C.).*

TABLE II.

No. of Experiments.	Time of exposure in hours.		Condition of Copper exposed.
	24	48	
1..... {	·04	·06	Clean.
	·05	·08	Sulphuretted.
2..... {	·04	·06	Clean.
	·05	·09	Sulphuretted.
Mean {	·04	·06	Clean.
	·05	·085	Sulphuretted.

This shows that results are obtained at (90—100° C.) similar to those at the ordinary temperature, the sulphuretted copper being more acted on than the non-sulphuretted metal.

Series III. *Exposed in Closed Flasks at the Ordinary Temperature.*—The results given in Tables I and II were thought to be due to the oxidation of the film of copper sulphide by the dissolved air to sulphate which would then dissolve, and this the following series of experiments prove to be the case, for in these experiments the water was previously well boiled and then placed in cork flasks, the latter being entirely filled with liquid.

TABLE III.

No. of Experiment.	Time of exposure, 48 hours.	Condition of Copper.
1.....	·14	Clean.
	·10	Sulphuretted.
2.....	·30	Clean.
	·24	Sulphuretted.
3.....	·25	Clean.
	·07	Sulphuretted.
Mean	·23	Clean.
	·14	Sulphuretted.

B. *Action of Saline Solutions.*

The solutions were placed in beakers and the copper exposed at the ordinary temperature for 48 hours. In Table IV the results obtained are given, from which it is seen that in every case previous treatment with ammonium sulphide lessens the action on the metal.

TABLE IV.

Grams salt in solution.	·001	·01	·05	·50	5·00	Condition of Copper.
KNO ₃	·10	·12	·12	·14	·81	Clean.
	·04	·04	·06	·06	·08	Sulphuretted.
NaNO ₃	·03	·08	·08	·10	·16	Clean.
	..	·02	·03	·07	·09	Sulphuretted.
K ₂ SO ₄	·28	·28	·29	·36	·54	Clean.
	·04	·08	·08	·12	·34	Sulphuretted.
MgSO ₄	·06	·10	·08	·04	·10	Clean.
	·04	·04	·04	·02	·06	Sulphuretted.
Na ₂ CO ₃	·16	·17	..	·50	Clean.
	..	·10	·10	..	·30	Sulphuretted.
K ₂ CO ₃	·14	·16	·18	..	·70	Clean.
	·08	·14	·14	..	·60	Sulphuretted.
NaCl	·16	..	2·40	Clean.
	·14	..	1·60	Sulphuretted.
(NH ₄) ₂ SO ₄	3·10	6·20	31·00	Clean.
	1·70	4·20	20·00	Sulphuretted.
(NH ₄)NO ₃	1·50	12·50	40·00	Clean.
	1·20	9·70	36·50	Sulphuretted.
NH ₄ Cl.	4·00	22·00	180·00	Clean.
	3·40	10·00	140·00	Sulphuretted.

We may conclude, then, from the above results, that previous washing with ammonium sulphide increases the action of distilled water on copper when exposed in open vessels, but lessens it when air is excluded, while in the case of saline solutions the action is diminished, even when air has free access.

XXIV.—On certain Bismuth Compounds. Part IV.

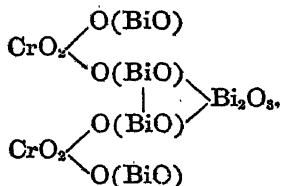
By M. M. PATTISON MUIR, F.R.S.E., Assistant Lecturer on Chemistry, The Owens College, Manchester.

1. IN a paper communicated to the Society and published in this Journal (vol. ii, 1876), I described a chromate of bismuth having the formula $(\text{BiO})_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (*monohydrated bismuthyl dichromate*). I described this salt as forming orange-yellow needles belonging to the monoclinic system (p. 19). These crystals have been more minutely examined under the microscope by my friend Dr. Burghardt, of this College, and he tells me that they belong to the orthorhombic system; he assigns to them the (probable) formula $\infty\text{P}\infty \cdot \infty\text{P.P.}$

2. In the third part of the present series of papers (vol. i, 1877, p. 24) I detailed the preparation and properties of another bismuth chromate, to which I assigned the formula $3\text{Bi}_2\text{O}_3 \cdot 7\text{CrO}_3$. I stated that the action of hot caustic potash upon this chromate results in the formation of a heavy, dark brown-red salt, a portion of the chromate being at the same time dissolved, with formation of a greenish-yellow liquid. I have prepared and analysed a further quantity of this new chromate: it is apparently identical in composition with the chromate described by Löwe (*J. pr. Chem.*, lxxvii, 288) as prepared by the addition of potassium dichromate solution to a nearly neutral solution of bismuth nitrate, viz., $3\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$. The reaction of hot caustic potash upon the chromate $3\text{Bi}_2\text{O}_3 \cdot 7\text{CrO}_3$ would thus appear to consist mainly in the withdrawal of part of the chromic acid as potassium chromate; the yellow colour of the liquid is doubtless due to the solution of the potassium chromate so formed—



The salt $3\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ may be regarded as $(\text{BiO})_4 \cdot 2\text{CrO}_4 \cdot \text{Bi}_2\text{O}_3$ (*bismutho-tetrabismuthyl dichromate*).



3. In the analysis of this chromate the bismuth was separated from the chromium in the form of oxychloride by the addition of a large quantity of warm water and a little ammonium chloride to the solution of the salt in hydrochloric acid. The chromium in the filtrate

was oxidised by boiling with bromine in alkaline solution, and was precipitated as barium chromate: the precipitate was gently warmed with a measured volume of ferrous sulphate solution of known strength, and the residual ferrous salt was determined by titration with potassium permanganate. The results were satisfactory. In former analyses of bismuth chromate I separated the bismuth by precipitation as sulphide, but I found that the precipitate invariably contained small quantities of chromium which could not be altogether removed by washing, and that solution in acid, followed by reprecipitation with sulphuretted hydrogen, was necessary in order to insure accurate results. The separation of bismuth by addition of a large volume of warm water is more readily accomplished, and yields very accurate results.

4. From my experiments upon the chromates of bismuth detailed in this and in preceding papers, it appears that the general action of acids upon these salts is to withdraw more or less bismuth, and so to form a salt comparatively richer in chromic acid than the original; alkalis, on the other hand, act by withdrawing chromic acid, and so producing a salt which contains a comparatively larger quantity of bismuth than the original. I have formulated the various chromates obtained by me, and briefly described the method of preparation of each in the following table. As my object is especially to show the relation existing between the amounts of bismuth and chromic acid in each, I have written the formulæ as if the salts were of the general composition $x\text{Bi}_2\text{O}_3 \cdot y\text{CrO}_3$:—

a. $3\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ (obtained by Löwe) by precipitating nearly neutral bismuth nitrate solution with potassium chromate.

b. $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$, by precipitating an acid solution of bismuth nitrate with potassium chromate.

c. $\text{Bi}_2\text{O}_3 \cdot \text{CrO}_3$, by boiling No. 2 with dilute nitric acid; also formed by treating No. 2 with alkali.

d. $5\text{Bi}_2\text{O}_3 \cdot 11\text{CrO}_3$, by prolonged heating of No. 2 with dilute nitric acid.

e. $3\text{Bi}_2\text{O}_3 \cdot 7\text{CrO}_3$, by treating No. 3 first with strong, then with dilute nitric acid.

f. $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$, by boiling No. 3 with strong nitric acid.

g. $3\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$, by action of hot caustic potash on Nos. 4 and 5.

5. In my last paper on bismuth compounds (vol. i, 1877, p. 28) I described the action of ammonia on bismuthous oxide, and on two oxybromides of bismuth, and I showed that this action results in the formation of metallic bismuth. I gave reasons for believing that at a temperature below redness, ammonia is decomposed by the salts of bismuth mentioned, and that the salts are then reduced by the hydrogen formed.

As corroborative of this hypothesis, and as opposed to the idea that a nitride of bismuth is alternately produced and decomposed in these reactions, I have observed that bismuthous oxide (Bi_2O_3) is unacted upon by dry nitrogen at temperatures varying from the ordinary temperature to that of red heat.

6. In former papers (vol. i, 1876, p. 149, and vol. i, 1877, p. 29) I have shown that the action of chlorine upon bismuthous oxide suspended in a concentrated boiling solution of caustic potash results in the production of hydrates of bismuth richer in oxygen than those corresponding with the trioxide itself. Of these hydrates the principal are $\text{Bi}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (x being a whole number, generally not greater than 2 or 3).

I find, on reference to a paper by Schrader (*Ann. Ch. Pharm.*, cxxi, 204), that this chemist was unable to prepare red bismuthic hydrate ($\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$) in a state of purity. The reddish-brown powder produced by the action of chlorine as described above was always found by Schrader to contain potash which could not be removed by washing; the addition of dilute nitric acid was insufficient to remove the whole of the potash, while concentrated acid brought about a partial decomposition of the hydrate, with production of $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The last-mentioned salt (hypobismuthic dihydrate) is described by Schrader as the final result of the action of hot concentrated nitric acid upon the mixture of higher hydrates of bismuth, produced by passing chlorine into a boiling concentrated solution of potash containing bismuthous oxide in suspension. Arppe (*Pogg. Ann.*, lxiv, 237) appears to have obtained bismuthic hydrate ($\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$) without difficulty by acting on the mixed hydrates containing potash with dilute nitric acid. In my former paper I stated that by warming the mixed hydrates with *concentrated* nitric acid for a few moments, the red bismuthic hydrate is readily obtained. This result I can now confirm. I have repeated the experiment, and find that there is no difficulty in preparing bismuthic hydrate, provided the caustic potash in which the bismuthous oxide is suspended be very concentrated; the passage of chlorine be maintained until the whole of the oxide is converted into a heavy, dense, chocolate-red powder; and this powder, after prolonged washing with boiling water, be gently warmed with concentrated nitric acid for a few moments, and then washed free from acid. If the action of the hot nitric acid be prolonged for some time, the red hydrate is gradually converted into an orange-yellow salt, part of the bismuth at the same time passing into solution. This orange-yellow salt, when dried over sulphuric acid, was found to be the hypobismuthic dihydrate ($\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) described by Schrader (*loc. cit.*).

7. I have examined the hydrate produced by precipitating a solution of bismuthic hydrate in concentrated hydrochloric acid by means of

caustic potash, and that formed by precipitating a solution of the same hydrate in concentrated sulphuric acid, by the same precipitant, after passing sulphur dioxide through the liquid.

(Bismuthic hydrate is very easily dissolved by concentrated hydrochloric acid with evolution of chlorine: concentrated sulphuric acid dissolves this hydrate only after prolonged digestion with it.)

In each case a very pale yellowish-white flocculent precipitate was obtained.

These precipitates were dried over sulphuric acid in a vacuum. That produced by precipitating the solution of bismuthic hydrate in hydrochloric acid I shall call A: the other I shall call B.

- A. 0.3652 gram gave 0.336 gram $\text{Bi}_2\text{O}_3 = 0.30155$ gram Bi.
 0.1093 gram lost 0.0073 gram when heated to 100° for two or three hours.
- B. 0.3353 gram gave 0.3225 gram $\text{Bi}_2\text{O}_3 = 0.2894$ gram Bi.
 I had not a sufficient quantity to determine the water.

A.

Calculated for $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.		Found.
Bismuth	83.33	82.58
Water	7.14	6.68

B.

Calculated for $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$.		Found.
Bismuth	86.42	86.34
Water	3.70	3.88 (by difference).

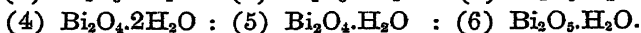
A. Suffered no further loss of weight on being heated to 180 — 190° . When exposed to the temperature of the Bunsen flame, the colour gradually changed to light yellow.

8. By solution in concentrated hydrochloric or sulphuric acid, bismuthic hydrate appears to lose oxygen: by precipitating these solutions no hypobismuthic hydrate, but a bismuthous hydrate is produced.

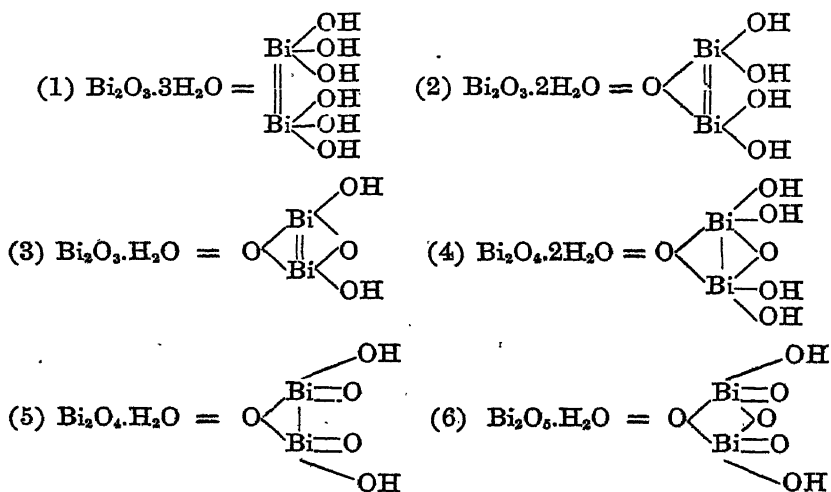
9. I have already (vol. i, 1876, p. 151) described experiments carried out with the view of ascertaining whether bismuthic hydrate contains hydrogen which may be replaced by metal. These experiments led to negative results. A similar attempt in the case of hypobismuthic hydrate was likewise attended with no positive result (vol. i, 1877, p. 30). I have supplemented these experiments by attempting to prepare a bismuthate or bismuthite of potassium by fusing bismuthous oxide, and metallic bismuth respectively, with caustic potash: in each case potassium carbonate and silicate (a porcelain

crucible was employed) were produced, but in neither instance did I succeed in obtaining traces of any substance which could possibly be regarded as a salt of bismuthic acid, or of any other oxyacid of bismuth. I conclude therefore that the hydrates of bismuth, so far as they have been examined, are devoid of acid properties.

10. The following hydrates of bismuth are now known :—

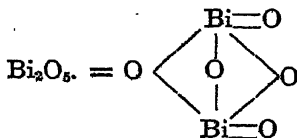


The relations existing between these hydrates, and between the hydrates and corresponding oxides may, I think, be advantageously shown by the following formulæ* :—



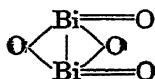
Passing from 1 to 2 and 3, we have a gradual replacement of hydroxyl by oxygen : in 4 this replacement is carried further, and in 5 further still : 4 and 5 are obtained from 1, 2 or 3 by the action of oxidisers. In 6 the replacement of hydroxyl is apparently carried to the farthest limit ; this hydrate is produced from the others by the action of very energetic oxidising agents : 6 readily goes back to 1, 2 or 3.

By replacing the hydroxyl groups in 6 by oxygen, we get bismuthic oxide—

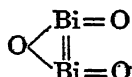


* Of course I do not mean to say that the formulæ given above are the true molecular formulæ for these hydrates ; they may or may not be so, but probably are not.

This oxide is easily reduced to bismutho-bismuthic or hypobismuthic oxide; at 150° it begins to give off oxygen, and at 250° is entirely reduced to Bi_2O_3 , which may be regarded as—



At 250° or so bismutho-bismuthic oxide is reduced to bismuthous oxide, which is the most stable oxide of the series. Bismuthous oxide may be regarded as hydrate 1, 2, or 3, in which the whole of the hydroxyl is replaced by oxygen—

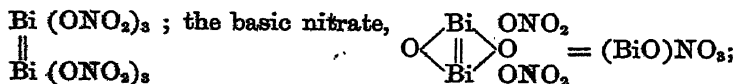


Lastly, a lower oxide, Bi_2O_2 , apparently exists; this oxide is said to be reduced with difficulty (Sehneider, *Pogg. Ann.*, lxxxviii, 45): it may, with propriety, be regarded as—

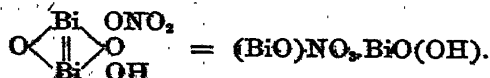


11. With reference to the existence of an oxide of bismuth lower than bismuthous oxide, I have observed, when igniting the latter oxide, that if the semi-charred filter-paper held on platinum wire be brought within a few millimeters of the surface of the hot oxide, the latter becomes covered with an ashen-grey film; on removing the filter paper, this film disappears. I have observed this fact so constantly, that I am certain it is not a mere accident, and I am also certain that the film is not due to the deposition of carbon from the paper. I am inclined to regard the ashen-grey film as consisting of a hypobismuthous oxide. I hope to be able, at a future date, to lay before the Society an account of more exact experiments upon the production of such an oxide.

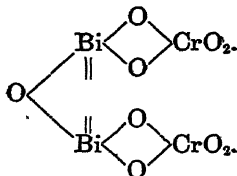
12. The greater number of the bismuth salts may be regarded as derived from one or other of the hydrates formulated in par. 10. The normal salts may perhaps be best viewed as derived from hydrate 1, and many of the so-called basic salts from hydrate 3. Thus the normal nitrate may be—



and the second basic nitrate—



A few salts may be derivatives of hydrate 2; for instance the dichromate obtained by Löwe (see this Journal, vol. ii, 1876, p. 19), may be formulated thus—



13. It is stated in Watts's Dict. (ii, 225) that "nitrate of bismuth forms with ferrocyanide of potassium a white, yellowish-white, or yellow precipitate, which afterwards turns green."

Thinking that a volumetric process for the estimation of bismuth might possibly be founded upon this reaction, I added ferrocyanide of potassium from a burette to a nearly neutral warm solution of bismuth nitrate, until a drop of the supernatant liquid produced a blue colour when spotted on filter-paper with ferric chloride. I found, however, that the process did not yield concordant results; that the temperature, and also the degree of neutralisation of the bismuth nitrate solution, largely conditioned the amount of ferrocyanide which it was necessary to add before obtaining the final reaction. On continuing to warm the liquid, the precipitate, which was at first of a very light green colour, gradually became darker, until finally it assumed the appearance of prussian blue. I was therefore induced to examine the precipitate more carefully.

14. When a solution of potassium ferrocyanide is added to a solution of bismuthous oxide in nitric acid containing just sufficient free acid to prevent precipitation of basic salts, an almost colourless, flocculent precipitate is produced. If the precipitation be effected in an open beaker, the precipitate quickly assumes a pale yellow colour, which passes after some time to an apple-green.

The precipitate settles very slowly; if it be collected on a filter and washed, it very quickly assumes a greenish colour. If the liquid containing the colourless, or slightly coloured precipitate be boiled, the changes in colour noticed above take place very rapidly: further, the apple-green precipitate becomes grass-green, then olive-green, then green-blue, and finally deep blue. The production of the final blue precipitate is hastened by adding a little nitric acid; the addition of a considerable excess of potassium ferrocyanide along with nitric acid causes an almost immediate production of this blue precipitate in the boiling liquid. If a hot solution of potassium ferrocyanide be added to a hot, nearly neutral solution of bismuth nitrate, contained in a flask, and the flask be quickly corked, a white precipitate is moment-

arily formed, but quickly becomes yellow, then green, and finally greyish-blue, the supernatant liquid remaining greenish-blue. If the cork be now withdrawn, the grey-blue precipitate slowly loses its grey tint, until it becomes of the colour of prussian blue, the supernatant liquid at the same time also becoming of a more decided blue colour. If the light green precipitate obtained as described be exposed to the air along with an excess of potassium ferrocyanide solution containing free nitric acid, it slowly darkens in colour; if the supernatant liquid be poured off and exposed to the air, it becomes more and more dark green in shade, and at the same time deposits a light greyish-blue precipitate. During the passage of the pale to the dark-coloured precipitates, hydrocyanic acid is invariably evolved. The blue supernatant liquid finally obtained gives the reactions of alkaline nitroprusside.

15. I prepared a quantity of the apple-green precipitate, by precipitating a nearly neutral cold solution of bismuth nitrate with excess of potassium ferrocyanide also dissolved in cold water, washed the precipitate repeatedly, as far as possible out of contact of air, and dried it at 100°. On shaking up the precipitate with hot water, a coloured liquid having an acid reaction was obtained; the process was repeated on the residue with the same result: hydrocyanic acid was evolved during the treatment with warm water.

On boiling the precipitate with water, hydrocyanic acid was evolved in considerable quantity, and a very decidedly acid liquid was obtained. This acid liquid contained small quantities of bismuth. The precipitate was very quickly decomposed by boiling with water containing a few drops of nitric or hydrochloric acid, hydrocyanic acid being copiously evolved, and the residue becoming much darker in colour. Quantities of the olive-green, green-blue, and deep blue precipitates were also prepared by boiling the apple-green solid with dilute nitric acid for longer or shorter periods, washing with water, and drying at 100°. Each of these precipitates was decomposed by boiling with water, with evolution of hydrocyanic acid, and production of a coloured and acid liquid. The more blue the colour of the precipitate, the less quickly, and the less completely did it undergo decomposition, by treatment with boiling water. These dark-coloured precipitates were partly soluble in strong nitric, or hydrochloric acid; the solutions contained bismuth. The precipitates were all decomposed by boiling with caustic soda or potash, oxides of bismuth and iron remaining, the former much predominating, and ferrocyanic acid going into solution: the solutions also contained traces of bismuth.

16. The apple-green precipitate prepared as already described, was submitted to analysis. I first endeavoured to decompose the salt by boiling it with caustic alkali and mercuric oxide, but I found that

although the whole of the bismuth was contained in the residue, a part of the iron passed into solution, and was precipitated, apparently as prussian blue, on adding sulphuric acid to the filtrate.

As concentrated sulphuric acid was found readily to decompose the apple-green salt, weighed quantities were warmed with this acid in basins until the greater part of the free acid was evaporated, the residue was washed into a beaker, mixed with a large quantity of warm water, and ammonia was added drop by drop until the whole of the bismuth was thrown down (see par. 21). The iron in the filtrate was reduced by means of pure zinc, and the ferrous salt determined by standardised permanganate. The precipitated bismuth salts were dissolved in nitric acid, and the bismuth was determined in this liquid. The cyanogen was determined by difference.

(a.) 0.5405 gram gave 0.273 gram Bi_2O_3 = 0.245 gram Bi.

(b.) 0.5405 gram required 7.7 c.c. permanganate = 0.067452 gram Fe. (1 c.c. permanganate = 0.00876 gram iron).

(c.) 0.709 gram gave 0.346 gram Bi_2O_3 = 0.3106 gram Bi.

(d.) 0.709 „ required 9.4. c.c. permanganate = 0.08235 gram Fe.

	I.	Found. II.	III.	IV.	V.	VI.
Bismuth ..	45.33	43.80	—	—	—	—
Iron	—	—	12.48	11.61	—	—
Cyanogen..	—	—	—	—	42.19	44.59

0.538 gram when heated to 130° for 3 hours lost 0.0199 gram = 3.69 per cent.

These numbers do not agree very closely: it is evident from the result obtained by heating the salt that a temperature of 100° was not sufficient to drive off the whole of the moisture. If the mean percentages of bismuth, iron, and cyanogen be calculated on the dry salt, the following numbers are obtained:—

Bismuth	46.26
Iron	12.52
Cyanogen	41.22
	<hr/>
	100.00

Assuming bismuth to be a pentad, the normal ferrocyanide would be $\text{Bi}_4\text{5FeCy}_6$: this formula requires—

Bismuth	44.21
Iron	14.74
Cyanogen	41.05
	<hr/>
	100.00

17. These numbers evidently point to the formula given above— $\text{Bi}_4\cdot5\text{FeCy}_6$ —as expressive of the composition of this apple-green salt: but the salt has plainly undergone partial decomposition by exposure to the air, and by the action of the wash water.

I therefore endeavoured to prepare a fresh quantity of bismuth ferrocyanide in a purer condition. For this purpose a cold solution of potassium ferrocyanide was added to a cold and nearly neutral solution of bismuth nitrate contained in a flask, which was almost filled with the liquids: the flask was then corked. When the precipitate had settled, the clear liquid was run off, the precipitate was thrown upon a filter, washed with water in an atmosphere of carbon dioxide, and dried over sulphuric acid *in vacuo*. Before becoming thoroughly dry, the precipitate was nearly colourless, being possessed of only a faint blue-green tinge. As the process of drying reached a close, a decided yellow-green colour was however developed. The following numbers were obtained on analysis:—

- (a.) 0.329 gram required 5.4 c.c. permanganate = 0.04731 gram Fe.
 (b.) 0.143 " " 2.3 " = 0.02015 "
 (c.) 0.143 " gave 0.07 gram Bi_2O_3 = 0.06282 gram Bi.
 (1 c.c. permanganate = 0.00876 gram iron).

Calculated for $\text{Bi}_4\cdot5\text{FeCy}_6$.		Found.			
		I.	II.	III.	IV.
Bismuth....	44.21	43.93	—	—	—
Iron	14.74	—	14.38	14.09	—
Cyanogen ..	41.05				(by difference) 41.56

These numbers show that the precipitate produced as described above, consisted of nearly pure bismuth ferrocyanide, $\text{Bi}_4\cdot5\text{FeCy}_6$.

18. By adding a cold solution of bismuth nitrate, which had been previously boiled, to a solution of potassium ferrocyanide in boiled water, a white precipitate was obtained, which after washing with cold water in a closed vessel, remained colourless. Bismuth ferrocyanide when pure is thus evidently a colourless salt. When dried over sulphuric acid, the precipitate became slightly coloured, owing, doubtless, to the action of the air upon it. If dried at 100° , the outer surfaces of the salt rapidly became covered with a more or less deep blue film, hydrocyanic acid being simultaneously evolved.

When the pale-yellow salt, obtained by drying over sulphuric acid, was heated to 150° or so it darkened in colour, and hydrocyanic acid was evolved; at 180° the salt was completely decomposed.

19. The olive-green salt produced by warming bismuth ferrocyanide with very dilute nitric acid was collected, dried at 100° , and analysed.

- (a) 0.4995 gram gave 0.195 gram $\text{Bi}_2\text{O}_3 = 0.175$ gram Bi.
 (b) 0.4928 " " 0.193 " " = 0.1732 " "
 (c) 0.4995 " required 9.2 c.c. permanganate = 0.0806 gram Fe.
 (d) 0.4928 " " 9.5 " " = 0.08322 " "
 (1 c.c. permanganate = 0.00876 gram iron):

	Found.			
	I.	II.	III.	IV.
Bismuth.....	35.04	35.15	—	—
Iron	—	—	16.14	16.89

When dried at 120—125° the salt lost 5.65 per cent. of moisture.

Calculating the foregoing percentages of bismuth and iron on the dry salt, we have—

	I.	II.	III.	IV.	V.
Bismuth..	37.14	37.30	—	—	—
Iron	—	—	17.11	17.85.	—
Cyanogen (by deducting mean of Bi + Fe from 100°)	45.30.				

The formula for normal bismuth ferricyanide (Bi being pentad), viz., Bi_5FeCy_6 , requires—

Bismuth	37.29
Iron	16.59
Cyanogen	46.12

which agree tolerably well with the numbers obtained.

I am inclined to regard this olive-green salt as bismuth ferricyanide containing small quantities of one or more products of decomposition of ferrocyanide (probably prussian blue) mixed with it.

If this view be correct, the first action of oxidising agents upon bismuth ferrocyanide would be to convert it, partially at any rate, into the corresponding ferricyanide. This is not different from what one would expect from the general relations existing between ferro- and ferri-cyanides.

By precipitating a cold solution of nearly neutral bismuth nitrate with excess of a cold solution of potassium ferricyanide I obtained a yellow-green precipitate having a tinge of brown; when washed with cold water, by decantation, in a closed vessel, this precipitate underwent no apparent change, but when dried at 100° the outer surface became covered with a greenish-blue film, while hydrocyanic acid was evolved. I hope to prepare a further quantity of this yellow-green salt (which is probably pure bismuth ferricyanide) and to examine its properties in detail.

20. A quantity of the green-blue substance, obtained by boiling the olive-green salt (impure ferricyanide) for some time with dilute nitric acid, was dried at 100° and analysed.

- (a) 0.410 gram gave 0.166 gram Bi_2O_3 = 0.149 gram Bi.
 (b) 0.392 " " 0.128 " " = 0.1149 " "
 (c) 0.392 " required 10.5 c.c. permanganate = 0.09198 gram Fe.
 (1 c.c. permanganate = 0.00876 gram iron).

	I.	Found. II.	III.
Bismuth	36.38	29.31	—
Iron	—	—	23.47

These numbers show very considerable discrepancies. These may, I think, be most probably accounted for by regarding the substance as a mixture of bismuth ferricyanide with varying amounts of the products of the decomposition of this salt by the action of nitric acid; of these products prussian blue is doubtless one.

As the decomposition proceeds with tolerable rapidity, it is not difficult to believe that the product should vary in composition throughout its mass. The deep-blue substance obtained by the continued action of hot nitric acid upon the green-blue powder was not quantitatively analysed: it contained small quantities of bismuth.

I propose to continue these investigations upon the ferro- and ferricyanides of bismuth, and hope to communicate the results to the Society at a future time.

21. In par. 16 of the present paper I stated that in the analyses of the ferrocyanides of bismuth, after decomposition by means of sulphuric acid and addition of water, the bismuth was entirely precipitated by addition of ammonia. I have found that it is possible to precipitate bismuth completely from a solution containing this metal along with iron by cautious addition of dilute ammonia; the precipitate contains the whole of the bismuth, while the filtrate contains the whole of the iron. On the first addition of ammonia a portion of the ferric salt is thrown down, but on shaking the liquid this is redissolved, and on continuing to add ammonia, with constant agitation, the iron remains in solution until the bismuth is entirely thrown down as oxide. The liquid remains distinctly acid after the last trace of bismuth has been precipitated.

Bismuth may be separated in the same way from chromium, aluminium, and manganese. If a solution containing bismuth be mixed with a few drops of ferric chloride solution and ammonia be then added, the point at which the whole of the bismuth is precipitated may be determined with the greatest accuracy, as immediately the last trace of bismuth is thrown down a reddish-brown colour is produced from the precipitation of ferric hydrate. I had hoped to have founded a volumetric method for estimating bismuth upon this reaction, but on trial I found it unavailable. Thus, a solution containing

0.07672 gram of bismuth in 50 c.c. of dilute nitric acid required 18.1 c.c. of dilute ammonia for complete precipitation; another solution, containing 0.038296 gram of bismuth in 50 c.c. of the same acid required exactly the same amount of the same dilute ammonia for complete precipitation.

ADDENDUM.

Since writing the above I have noticed a paper by M. Wyrouboff, entitled "Researches on the Ferrocyanides" (*Ann. Chim. et Phys.* [5], viii, 444), in which, among other salts, two ferrocyanides of bismuth are described. One of these is produced by adding a solution of potassium ferrocyanide to a solution of bismuth nitrate containing little free acid. The salt is said to be of a yellow colour, inclining to green: when washed and dried it does not undergo decomposition. It is slightly soluble in water. The formula $\text{BiKFeCy}_6 \cdot 4\text{H}_2\text{O}$ is assigned, apparently on the evidence of a single estimation of bismuth, iron, and potassium; no numbers, other than the calculated percentages, are given. From the experiments detailed in the preceding paragraphs of this paper it is, I think, evident that M. Wyrouboff worked with an impure ferrocyanide of bismuth; he had not washed it free from potash; and he had allowed it to undergo partial decomposition by the action of the free acid present. I find that ferrocyanide of bismuth begins to decompose at temperatures over 150° . The salts prepared by me and dried over sulphuric acid did not lose more than from 3 to 4 per cent. of their weight when heated to about 150° for some hours. The formula assigned by M. Wyrouboff to bismuth ferrocyanide requires 14.5 per cent. of water; no estimation of water is given in M. Wyrouboff's paper.

To the second ferrocyanide of bismuth the formula $\text{Bi}_2\text{FeCy}_6 \cdot 5\text{H}_2\text{O}$ is assigned: it is said to be produced by using ferrocyanhydric acid as precipitant in place of potassium ferrocyanide, and to resemble the first-mentioned ferrocyanide in all respects. In this salt bismuth, says M. Wyrouboff, is divalent. One estimation of iron and one of bismuth appears to have been made. This salt may exist, but it seems to me that the author of the paper should have taken more pains, and carried out a greater number of analyses, before publishing his results, especially before even hinting that he looked on bismuth as by turns, di- and tri-valent. In fact, any conclusions concerning quantivalence, deduced from a study of compounds in the solid state, must, in the present state of our knowledge, be almost valueless.

XXV.—*Additional Note on a Process for Estimating Bismuth Volumetrically.*

By M. M. PATTISON MUIR, F.R.S.E.

1. IN the course of last session I communicated to the Society the details of a process for the volumetric estimation of bismuth (*Chem. Soc. J.*, vol. i, 1876, p. 483). This process was founded upon the facts that potassium dichromate precipitates bismuth from slightly acid solutions in the form of bismuthyl dichromate, and that potassium dichromate gives a red precipitate with silver nitrate. By taking advantage of these facts, and by employing a standardised solution of potassium dichromate, it becomes possible to estimate bismuth with very considerable accuracy.

2. In order to obtain a solution of a bismuth salt, which should be but slightly acid, I added ammonia to a solution of bismuthous oxide in nitric acid until a faint cloudiness appeared in the liquid. Although I obtained tolerably satisfactory results when working with this process, I nevertheless felt that the risks of error were by no means small. If too little ammonia was added a very considerable excess of dichromate was required before the whole of the bismuth was precipitated: if too much ammonia was added, part of the bismuth was thrown down as hydrate; the results were in both cases rendered inaccurate.

I have made several attempts to remedy this defect in the process, and have, I think, at last succeeded in doing so.

3. An acid solution of bismuth nitrate is precipitated by addition of excess of sodium acetate: the precipitate is soluble in nitric acid. If ammonia be cautiously added to this solution, it is easy to reach a point at which a faint cloudiness, but no distinct precipitate, is produced in the liquid.

If this liquid be boiled, a precipitate quickly forms, which again disappears on adding nitric acid drop by drop to the boiling solution. If potassium dichromate be now added, the whole of the bismuth is thrown down. The results obtained were very satisfactory.

4. The method which I have finally adopted differs somewhat from the foregoing: it is based upon the facts that the precipitate produced by excess of sodium acetate in a solution of a bismuthous salt in excess of nitric acid, is easily soluble in acetic acid, that this solution yields no precipitate on boiling, but that the addition of potassium dichromate to the hot liquid causes the deposition of the bismuth in the form of a yellow chromate (probably bismuthyl dichromate, $(\text{BiO})_2\text{Cr}_2\text{O}_7$).

I have carried out a number of experiments by the modified method, and have obtained exceedingly concordant results. I do not propose to detail the numbers obtained, as my former paper contained a suffi-

ciency of analytical results to enable one to form an opinion concerning the general accuracy of the method.

5. I now carry out the volumetric estimation of bismuth as follows :—A solution of recrystallised potassium dichromate, containing about 10 grams of the salt in 1,000 c.c. of water, is prepared. A known weight of pure bismuthous oxide, (Bi_2O_3), is dissolved in excess of nitric acid, and a solution of sodium acetate is added to this liquid until a copious white precipitate is thrown down; acetic acid is then added in quantity sufficient to dissolve the precipitate completely, and to insure that, when the liquid is made up with water to a fixed volume, say to 250 c.c., no precipitate shall be formed. A certain volume of this liquid is withdrawn by means of a pipette, placed in a beaker, and heated to boiling; the potassium dichromate is then gradually run in from a burette, the liquid being boiled between each addition of the solution, until a drop of the supernatant liquid gives a faint reddish-brown coloration when spotted with silver nitrate on a white slab.

6. Experiments have proved that the addition of a slight excess of acetic acid does not interfere with the accuracy of the results; a large excess of the acid must, however, be avoided. Dilution of the liquid after addition of acetic acid does not influence the results, provided that such dilution be not carried so far as to produce turbidity in the liquid, either when cold or when raised to the boiling point. In using the standardised dichromate, a process similar to that sketched above is pursued.

7. I have shown in another paper ("On certain Bismuth Compounds," Part IV), that bismuth may be separated from iron, aluminium, chromium, and manganese, by adding ammonia to the acid liquid containing these metals. It is well known that bismuth is precipitated as an oxy-salt by addition of much water to a solution containing this metal, provided that free acid be present in moderate excess only.

Applying these facts, it becomes easy to estimate bismuth volumetrically in the presence of most of the more commonly occurring metals, with the exception of those of the arsenic group. It is only necessary to partially neutralise the acid liquid by addition of ammonia, to add a considerable quantity of warm water along with a little sodium or ammonium chloride, to wash the precipitate with warm water, to dissolve it in nitric acid (filtering from insoluble silver chloride if necessary), to add excess of sodium acetate, followed by addition of such a quantity of acetic acid as serves to completely dissolve the precipitate which has been produced, and to titrate with standardised potassium dichromate. If much lead be present it will be advisable to remove it, by boiling down the original liquid with sulphuric acid, before precipitating with water and a soluble chloride.

XXVI.—On the Solvent Action of various Saline Solutions upon Lead.

By M. M. PATTISON MUIR, F.R.S.E., Assistant Lecturer on Chemistry, The Owens College, Manchester.

1. I HAVE published in the Proceedings of the Literary and Philosophical Society of Manchester a series of papers upon the solvent action of dilute saline solutions upon lead (*Proc.*, 1875-76, p. 35; 1876-77, pp. 1 and 142).

In these papers I have endeavoured to determine the circumstances conditioning the solvent action of the saline solutions experimented with.

In the present note I wish to examine these experiments, and others to be hereafter detailed, with the view of ascertaining, if possible, the chemical action which occurs when lead undergoes solution by liquids containing various salts.

2. In the following table I have arranged a few of the results obtained, with the view of showing the order in which the salts examined exert a solvent action upon lead. The lead used was sold as "pure:" it contained small traces of manganese, zinc, and iron. The experiments are arranged in three divisions.

A. Experiments carried out in Corked Flasks.

Salt.	Grams per litre.	Surface of lead exposed in sq. cm.	Total lead in mgms. in solution, after 14—21 days.	
Ammonium nitrate ..	0·20	25	1·8	1·8
Potassium ditto	"	"	1·2	1·6
Calcium chloride	"	"	1·9	3·0
Ammonium sulphate.	"	"	0·7	0·7
Potassium carbonate.	"	"	0·3	0·3

B. Experiments carried out in Beakers, covered with Porous Paper.

Diam. of mouth of Beaker = 11·5 cm.

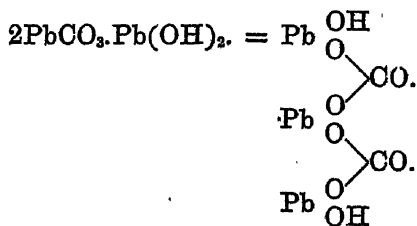
Ammonium nitrate ..	0·20	25	2·0	4·0
Potassium ditto	"	"	0·4	0·5
Calcium chloride	"	"	1·6	2·8
Ammonium sulphate.	"	"	1·1	1·3
Potassium carbonate.	"	"	0·3	0·3

C. *Experiments carried out in Basins, covered with Porous Paper.**Diam. of mouth of Basin = 14.5 cm.*

Ammonium nitrate ..	0.20	25	8.0	16.0
Potassium ditto	„	„	2.8	6.0
Calcium chloride	„	„	3.2	5.5
Ammonium sulphate.	„	„	9.2	16.0
Potassium carbonate.	„	„	0.7	0.7

It is evident that the quantities of lead dissolved by the same saline solution vary considerably, according as air has or has not free access to the surface of the liquid. More lead is generally dissolved when large surfaces of liquid are exposed to the air, than when small surfaces are exposed. Taking the results as a whole, the salts may be arranged in the following order, in which that salt exerting the most notable solvent action is placed first:—Ammonium nitrate, calcium chloride, ammonium sulphate, potassium nitrate, potassium carbonate.

3. The deposit which formed on the surface of the exposed lead, and on the bottom of the vessels, was collected, examined, and shown to be a hydrated lead carbonate: the results of analysis agreed most closely with the formula—



The hydrocarbonate presented the appearance of fine silky scales; the same salt has been obtained by Miller and others.*

4. A quantity of the hydrocarbonate was collected and washed; its solubility in dilute solutions of the salts enumerated in the foregoing tables, was then determined. This was done by shaking up an excess of the salt with the various solutions, and determining the lead dissolved at the expiry of fixed periods, by the colorimetric method described by me in the Proceedings of the Manchester Society (1875-76, p. 31). The following table contains the results.

* In the course of an experiment with this salt, I found that the whole of the lead contained in a solution made strongly alkaline by caustic potash, was precipitated by the addition of metallic aluminium.

A. *Experiments in Corked Flasks, each containing 500 c.c. of liquid.*

Salt.	Grams per litre.	Total lead in solution in mgms.			
		after	2	4	7 days.
Distilled water			trace	trace	trace
Potassium carbonate	0.20		none	none	none
Ditto nitrate	"		1.5	1.5	1.5
Ammonium ditto.....	"		3.0	9.5	9.5
Ditto sulphate.....	"		1.3	1.3	1.3
Calcium chloride.....	"		1.8	1.8	1.8
Distilled water saturated with CO ₂ at ordinary temperature and pressure	}		10	10	10

B. *Experiments in Beakers, covered with Porous Paper, each containing 500 c.c. of liquid.*

Distilled water		trace	trace	trace
Potassium carbonate	0.20	none	none	none
Ditto nitrate	"	1.1	1.1	0.7
Ammonium ditto	"	1.5	1.5	1.3
Ditto sulphate.....	"	1.0	1.0	0.8
Calcium chloride.....	"	1.5	1.5	1.3
Distilled water saturated with CO ₂ at ordinary temperature and pressure	}	10	10	10

5. About 200 c.c. of distilled water, saturated with carbon dioxide at the ordinary temperature and pressure, were now added to each solution, with the exception of the ammonium nitrate solution contained in the flask. After 24 hours the quantities of lead in solution were determined; in each case the amount had increased at least three-fold.

I have elsewhere shown that water charged with carbon dioxide at the ordinary temperature and pressure exerts very little solvent action upon metallic lead immersed in it, but that large quantities of lead are dissolved by water which has been charged with the same gas under a pressure of about 6 atmospheres (*Manch. Proc.*, 1875-76, p. 39).

6. The cork was withdrawn from the flask containing the ammonium nitrate solution, and the mouth of the flask was covered with porous paper: the quantity of lead in solution was determined at intervals of two or three days. The results were as follows:—

Total Lead in Solution in mgms.		
after 2	4	6 days.
9	7	6.5

In the last paper communicated to the Manchester Society I have detailed experiments wherein large quantities of lead were dissolved by various solutions when these were placed in corked flasks. So soon, however, as the liquids holding lead in solution were freely exposed to the air, the lead began to be thrown down in the form of hydrocarbonate. Miller obtained similar results.

7. I found, as a general rule, that the greater the quantity of lead dissolved by the action of saline solution upon the metal, the less was the quantity of lead hydrocarbonate deposited upon the containing vessel.

8. The experiments which I have described lead to the following conclusions:—

(a.) Lead hydrocarbonate is more soluble in the liquids examined when air has not free access to these liquids.

(b.) This salt is much more soluble when carbon dioxide is added in quantity. This agrees with the result formerly obtained by Miller.

(c.) A solution of potassium carbonate (and probably of other carbonates) exerts no solvent action upon the salt.

(d.) Lead hydrocarbonate is slowly deposited from its solutions in various saline liquids, by the action of air upon these liquids; the final precipitation of the salt takes place very slowly from solutions containing ammonium nitrate.

(e.) The order of solubility of lead hydrocarbonate in the various liquids examined, corresponds tolerably with the solubility of metallic lead in the same liquids.

In a long series of experiments I found that generally (not invariably) the maximum amount of lead is dissolved by saline solutions acting upon the metal when air has free access to the surface of the liquids.

9. Putting the whole of my results together, I draw the general conclusion that the action upon lead of those saline solutions which I have examined, results in the first place in the production of a salt other than the hydrocarbonate: that carbon dioxide is slowly absorbed from the atmosphere, and that the soluble lead compound is thereby slowly converted into hydrocarbonate, in which state it is to a greater or less degree precipitated: that in certain liquids (especially in those containing ammonium nitrate and calcium chloride) the formation of the soluble lead salt proceeds more rapidly than its decomposition into hydrocarbonate; but that after long periods of time the latter action generally begins to preponderate over the former: and, lastly, that carbonates reprecipitate the soluble lead salt (whatever it may be) as fast as it is produced, in the form of hydrocarbonate.

10. The belief that, after long periods, the formation and precipitation of hydrocarbonate preponderates over the formation of the soluble

salt is borne out by results obtained by exposing lead to the action of various solutions for periods amounting to 62 days. I may quote a few of the numbers.

Salt.	Grams per litre.	Surface of lead exposed in sq.cm.	Total lead in solution, in mgms. after days.			
			6	15	38	62
Potassium carbonate	0.20	50	trace	trace	trace	small trace.
Ditto nitrate	"	"	1.20	1.00	0.50	0.40
Ammonium nitrate	"	"	2.50	1.00	0.80	0.60

11. The fact that water charged with carbon dioxide exerts a very slight solvent action upon lead, while the same water dissolves comparatively large quantities of lead hydrocarbonate, is, I think, explained by supposing that the large excess of metallic lead present in the former case reacts upon the soluble salt produced (perhaps a bicarbonate), and converts it again into the insoluble hydrocarbonate, while in the latter case there is always present a large excess of carbonic acid, and, under these conditions, the soluble carbonate is stable.

12. I have calculated the solubility of lead hydrocarbonate in the various saline solutions experimented with: the results can only be looked upon as approximate.

On account of the very small quantity of salt in each solution, I have assumed the specific gravity of the liquid to be equal to that of pure water.

Solubility of Lead Hydrocarbonate $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ in various dilute Saline Solutions at ordinary temperatures.

Solution.	Grams of salt per litre.	Solubility of lead salt.	
		Experiments carried out in corked flasks.	Experiments in beakers.
Ammonium sulphate .	0.20	1 part in 32,000.	1 part in 43,000.
Potassium nitrate. . . .	0.20	1 " 26,000.	1 " 43,000.
Calcium chloride	0.20	1 " 23,000.	1 " 26,000.
Ammonium nitrate ..	0.20	1 " 4,600.	1 " 26,000.
Water saturated with CO_2 .		1 " 4,300.	1 " 4,300.

VII. Notes on Madder Colouring Matters.

By EDWARD SCHUNCK, Ph.D., F.R.S., and HERMANN ROEMER, Ph.D.

WE propose in these notes to give an account of some recent experiments on colouring matters derived from madder, which were undertaken by us, for the purpose of elucidating some points which are still involved in obscurity. We shall not attempt to give a systematic arrangement to the account, but simply describe the results as they were obtained.

1. Detection of Small Quantities of Alizarin in Mixtures of Alizarin and Purpurin.

It is well known that alizarin and purpurin may be recognised by means of their absorption-spectra, even when only minute quantities of either substance, pure or impure, are examined. In the case of a mixture of both substances it is easy to discover purpurin in the presence of much alizarin, but not so if the purpurin greatly preponderates. If the amount of alizarin present is less than 5 p.c., the ordinary optical method does not suffice for its detection. Alkaline solutions of purpurin show a much greater power of absorption than do those of alizarin. That of the former extends, with a certain degree of concentration, to that part of the spectrum at which the bands of alizarin lie. If the amount of alizarin present in the mixture is below 5 p.c., its characteristic bands do not appear on diluting the solution.

The known methods of separating alizarin from purpurin are not to be depended on, and give, especially when operating on small quantities, unsatisfactory results. In any case it is necessary to crystallise repeatedly from alcohol, in order to obtain each substance in a state of purity. Purpurin is soluble in boiling alum-liquor, but it frequently occurs that all or nearly all the purpurin is deposited as the solution cools, in combination with alumina, instead of remaining in solution, as is generally asserted. Alizarin is also soluble in boiling alum-liquor, but far less so than purpurin, and is always deposited on the solution cooling and standing.

The different behaviour shown by alizarin and purpurin when their solutions in caustic alkali are exposed to the air, affords an easy means of detecting the minutest quantities of alizarin in a mixture of the two. In making the experiment, the mixture is dissolved in caustic soda-lye, and the solution is left exposed to the air in a shallow

vessel until it has become almost colourless, and the absorption-bands of purpurin are no longer seen on the addition of more alkali. During this process the purpurin is decomposed, the alizarin remaining unchanged. The latter is set at liberty by adding an excess of hydrochloric acid, and is then taken up by ether. It may now be easily recognised by its absorption-spectrum, which is not in the least affected by the products resulting from the decomposition of the purpurin. By this method it is possible to detect alizarin in 0.005 gm. of a mixture of purpurin and alizarin, containing 1 p.c. of the latter.

2. *Purpuroxanthic Acid, a Colouring Matter found in Commercial Purpurin.*

In preparing pure purpurin by treating the commercial product with boiling alum-liquor, adding hydrochloric acid to the solution and treating the precipitate produced by the acid with boiling alcohol, we observed that a portion of the precipitate remained undissolved in the form of a brown powder containing alumina. By treating this powder with boiling alcohol, to which a little hydrochloric acid was added, it dissolved, yielding a small quantity of a crystallised substance which was free from purpurin and was not identical with any of the substances accompanying purpurin described by Schützenberger and Schiffert. We propose to call it *purpuroxanthic acid*.

Having crystallised our purpurin from boiling alcohol, we examined the mother-liquor, and found it to contain an additional quantity of the new substance, along with purpurin, alizarin, purpuroxanthin and a small quantity of a body soluble in boiling baryta-water, which we have not been able to identify. The residue left on evaporation of the liquid was treated with boiling water, in which purpuroxanthic acid dissolves much more readily than the other substances. The filtered liquid gave, on addition of hydrochloric acid, an abundant orange-coloured precipitate which was filtered off and treated with boiling baryta-water, in order to remove the purpuroxanthin and the unknown body accompanying it, the barium purpuroxanthate remaining undissolved. The latter was decomposed with hydrochloric acid, and the purpuroxanthic acid set at liberty was crystallised from boiling alcohol. The traces of alizarin and purpurin accompanying it remained in the alcoholic mother-liquor. After two or three crystallisations from glacial acetic acid, its melting point became constant. It had exactly the same properties as the substance prepared from the alumina compound mentioned above.

Purpuroxanthic acid possesses properties by which it may readily be distinguished from pseudopurpurin, purpuroxanthin, and the other colouring matters described by Schützenberger and Schiffert. It

melts at 231° . At 232 — 233° , however, it splits up into purpuroxanthin and carbonic acid, and it is therefore hardly possible to sublime it without decomposition. The gas evolved during fusion gives a white precipitate when passed into lime water, while the residue has the properties of purpuroxanthin, the melting point being 264° . No other products are formed. Purpuroxanthic acid is more soluble in boiling water than most madder colouring matters. The solution has a yellow colour, and deposits crystalline flocks on standing. It dissolves easily in hot spirits of wine, giving a yellow solution, which on cooling deposits yellow lustrous needles. These needles, on exposure to the air, gradually become dull, apparently from loss of water of crystallisation. Concentrated alcoholic solutions however frequently yield crystalline plates, which retain their lustre on heating, and are therefore probably anhydrous. The substance dissolves easily in glacial acetic acid on boiling, giving a yellow solution with a slight green fluorescence, which on cooling deposits yellow shining micaceous scales resembling iodide of lead. Dilute solutions deposit on standing long crystalline needles of a deep yellow or reddish-yellow colour. On one occasion we obtained in place of needles flat triangular plates, which on drying became completely opaque. Purpuroxanthic acid is soluble in ether, chloroform and benzene. It dissolves in concentrated sulphuric acid, giving an intensely yellow solution, which shows no absorption-bands. It is easily decomposed on treatment with boiling nitric acid of ordinary strength. It dissolves in caustic potash, yielding a solution resembling in colour alkaline solutions of purpuroxanthin, but with a more decided red tinge; it shows no trace of absorption-bands. When treated for some time with boiling caustic potash-lye, purpuroxanthic acid yields purpurin, but whether purpuroxanthin is formed as an intermediate product we have not been able to ascertain. It is quite insoluble in baryta- and lime-water. The ammoniacal solution gives red precipitates with the chlorides of barium and calcium. An alkaline solution gives with alum a precipitate which dissolves completely in an excess of boiling alum-liquor, yielding a yellow solution which is not fluorescent, and shows no absorption-bands; on standing it deposits a quantity of orange-coloured flocks. The substance dissolves in boiling concentrated perchloride of iron solution, with a deep reddish-brown colour, and is reprecipitated by hydrochloric acid in yellow flocks. The alcoholic solution gives with acetate of lead an orange-coloured precipitate, the supernatant liquid being colourless. Since purpuroxanthin is not precipitated from its alcoholic solution by acetate of lead, the two substances may by this means be distinguished as easily as by the difference in their barium compounds. Purpuroxanthic acid in a freshly precipitated state dyes alumina mordants an orange and iron

mordants a brown colour. These colours are, however, very fugitive, and disappear entirely on treatment with boiling soap-liquor.

On comparing this description with the account given by Rosenstiehl of his ϵ -purpurin (*Compt. rend.*, lxxxiii, 827), it will be found that in most respects the two substances exactly coincide. In two particulars only will any essential difference be observed, the ϵ -purpurin being described as an orange-coloured powder, and its melting point given at 180° .

The analysis of our substance dried at 120° led to the following results:—

I. 0.2374 grm. of substance gave 0.5482 grm. of CO_2 and 0.0638 grm. H_2O .

II. 0.2264 grm. of substance from a different preparation gave 0.5222 grm. CO_2 and 0.0644 grm. H_2O .

III. 0.2526 grm. of substance prepared on a third occasion gave 0.5836 grm. CO_2 and 0.0720 grm. H_2O .

These numbers lead to the following composition:—

		Calculation.	I.	II.	III.
C_{15}	180	63.38	62.98	62.90	63.01
H_8	8	2.82	2.98	3.16	3.16
O_8	96	33.80	—	—	—
	<hr/> 284	<hr/> 100.00			

The formula $\text{C}_{15}\text{H}_8\text{O}_8$ or $\text{C}_{14}\text{H}_7\text{COOH}\text{O}_4$, to which these analyses lead, explains the decomposition of the substance into purpuroxanthin and carbonic acid, since



a process similar to that which other acids of the aromatic series, such as hydroxybenzoic acid, undergo under the same circumstances.

The small quantity of substance at our disposal (the purpurin employed in its preparation containing only about 1 p.c.) was not sufficient for the preparation of any compounds.

We propose making experiments to obtain it synthetically, proceeding from a bioxyanthraquinone. We think it probable that it is formed by the oxidation of some body pre-existing in the plant.

3. *Munjistin, ϵ -Purpurin and Purpuroxanthic Acid.*

We owe to the kindness of Dr. Stenhouse a specimen of munjistin, the beautiful substance discovered by him several years ago in Munjeet. We found it to bear a striking resemblance to the body described by us in the preceding note, and on examination discovered that its principal properties were exactly those of purpuroxanthic acid.

On being heated it began to soften at 225° , and fused completely at 230° . When further heated it evolved carbonic anhydride, and was converted into purpuroxanthin. By fusion with caustic alkali it yielded purpurin. Hence there can be little doubt that munjistin and purpuroxanthic acid are identical. The analyses of Dr. Stenhouse differ however considerably from ours, and we therefore propose to re-examine munjistin from munjeet in order to remove all doubts as to its identity with our substance.

Some time ago M. Rosenstiehl (*Compt. rend.*, lxxxiii, 827) described, under the name of *ε-purpurin*, a body which he found accompanying pseudopurpurin in a commercial product. This body, which he considers as a fifth isomeric of purpurin, may be formed, according to him, by the simple oxidation of purpureoxanthin, into which it is reconverted by reducing agents. By fusion with caustic potash it yields ordinary purpurin, in consequence of some internal molecular change. Although the properties of this substance strongly resemble those of purpuroxanthic acid, we did not venture to suppose the two bodies could be identical, since the behaviour of his *ε-purpurin*, as given by Rosenstiehl, was in many respects so different, that we were compelled to conclude they must be distinct. In a recent note (*Compt. rend.*, lxxxiv, 559), however, Rosenstiehl admits that *ε-purpurin* and purpuroxanthic acid are the same body, and that our view of its composition explains the reactions observed in a more satisfactory manner than his own. Having maintained that our substance has already been observed, which we by no means deny, Rosenstiehl proceeds to say, that it is identical with the madder orange of Runge. This is quite possible, since many of the properties of madder orange, as described by the discoverer, resemble those of purpureoxanthic acid. The process of preparing it given by Runge (*Journ. f. prakt. Chem.*, v, 362) is however one that under varying circumstances might yield different substances, and when repeated by one of us many years ago, it gave in fact, not purpuroxanthic acid, but rubiacin, a colouring matter, which according to the researches of Stenhouse and Stokes (*Proc. Roy. Soc.*, xii, 363), differs essentially from munjistin.

M. Rosenstiehl is of opinion that our substance is or may be formed from pseudopurpurin, for which he now gives a new formula, based on the assumption that it is decomposed on heating into purpurin and carbonic anhydride. By heating pseudopurpurin to 180° , Rosenstiehl finds that it does indeed evolve carbonic anhydride, and that it therefore belongs to the same class of compounds as purpuroxanthic acid. We rejoice to hear that the further investigation of this somewhat anomalous body, of which so little is known in spite of numerous researches, is in such able hands. Having, however, been the first to discover, among this series of bodies, one containing

a carboxyl group, we for our part claim to be left, for the present, in undisturbed possession of the field we have opened up, *i.e.*, the preparation and examination of such members of the series as are formed from alizarin and its isomerides, as well as from the isomerides of purpurin, by the replacement of H by COOH.

4. *Purpurin.*

Since its discovery by Robiquet, nearly fifty years ago, purpurin has been the subject of numerous investigations. The accounts given of its properties and composition by various chemists differ however very considerably. The analyses, with the exception perhaps of those of Schützenberger and Schiffert, indicate a more or less considerable admixture of alizarin. Graebe and Liebermann were the first to remove all doubts regarding the formula of purpurin, by showing that it is a derivative of anthracene, and must be considered as a trioxyanthraquinone. The methods formerly adopted for separating alizarin and purpurin were indeed imperfect, and though chemically pure alizarin had previously been obtained by the decomposition of its glucoside, it was only after the introduction of Kopp's method of preparation that chemists were enabled to procure purpurin in large quantities in a state of tolerable purity. Commercial purpurin however still contains a certain amount of alizarin, besides several other impurities. Even in a specimen which had been purified in the manufactory of Kahlbaum at Berlin by solution of the crude product in boiling alum liquor, we were able to detect traces of alizarin by the method described by us in a previous note. By again treating this product with boiling alum liquor, adding acid to the filtered solution, and dissolving the precipitated purpurin in boiling alcohol, we obtained a pure crystallised substance. Pure purpurin cannot be obtained by sublimation from the crude product, since alizarin sublimes at nearly the same temperature as purpurin.

The properties of purpurin have not been so minutely and accurately described as would seem desirable in the case of a body, of which several isomerides are already known. We have therefore ourselves carefully examined its properties, taking for the purpose a specimen of which the melting point remained constant after it had been converted into the acetyl-compound and again liberated. An analysis of the substance yielded the following results:—

0.2336 grm. of substance dried at 110° gave 0.5596 grm. CO₂, and 0.0736 grm. H₂O, corresponding in 100 parts to—

C	65.33
H	3.47

The formula $C_{14}H_8O_6$ requires—

C.....	65.62
H.....	3.12

Purpurin dissolves easily in boiling spirits of wine, yielding a yellow solution, from which it crystallises on cooling in thin flattened prisms, sometimes 3 millims. long, having a deep orange colour and much lustre. On being heated at 100° , these crystals become dark red from loss of water. From a solution of purpurin in strong alcohol dark red needles are deposited, which are anhydrous.

The determination of the water of crystallised purpurin led to the following results :—

0.4602 grm. of substance dried over sulphuric acid lost on being heated at 110° 0.0802 grm. $H_2O = 6.56$ p.c.

0.4110 grm. of substance lost 0.0260 grm. $H_2O = 6.32$ p.c.

The formula $C_{14}H_8O_6 \cdot H_2O$ would require a loss of 6.56 p.c., and the crystals therefore contain 1 molecule of water.

The melting point of purpurin is at 253° . It begins however to sublime at 150° (according to Schützenberger at 250°). The sublimate consists of red, plumose or needle-shaped crystals. Much carbonaceous residue is left. The crystals obtained by dissolving sublimed purpurin in spirits of wine are generally anhydrous, but occasionally hydrated crystals of the usual appearance are obtained. After purpurin has been repeatedly sublimed, its melting point becomes considerably depressed, indicating some kind of decomposition, but after recrystallising several times from alcohol, the melting point again becomes constant at 253° .

Purpurin is slightly soluble in boiling water, the solution having a yellow colour with a tinge of red, and depositing crystalline yellow flocks on cooling. It dissolves in ether, giving a yellow fluorescent solution, which shows two bands of absorption, as described by Professor Stokes (*Chem. Soc. Journ.*, xii, 219). It also dissolves readily in boiling carbon disulphide, benzene and glacial acetic acid, yielding yellow solutions which deposit crystalline needles on cooling. These solutions show two bands of absorption coinciding with those of the ethereal solution. Purpurin dissolves in concentrated sulphuric acid, giving a rose-red solution, which shows three bands of absorption, one in the yellow, the others in the same position as those of the ethereal solution. Purpurin dissolves in caustic potash and soda-lye, in sodium carbonate solution, and in ammonia. The solutions have a deep red colour, inclining to purple, and show the absorption-bands described by Professor Stokes and other observers. In alcoholic potash or soda, purpurin is almost insoluble. On being treated with boiling baryta-water, it forms a purple lake quite insoluble in water.

By treatment with lime water it yields a compound which resembles that with barium, and is also insoluble.

A solution of purpurin in caustic alkali loses its colour on exposure to the air, becoming pale yellow, and the purpurin disappears entirely. Vogel (*Deut. Chem. Ges. Ber.*, x, 159) ascribes the change which takes place in this case to the sensitiveness of the solution towards light, and thinks it is due chiefly to an absorption of the yellow rays. There can be little doubt however that the decomposition of the purpurin is caused by oxidation, since the alkaline solution remains unchanged for weeks, if kept in a well stoppered bottle even on exposure to direct sunlight, whereas the same solution soon becomes decolorised on exposure in an open vessel in the dark. If the solution be left to stand in a test-tube, it will be seen that the change of colour commences at the surface and proceeds gradually downwards.

On treatment with boiling alum-liquor, purpurin dissolves, giving the well-known pink fluorescent solution, the optical properties of which have been frequently described. The solution, on cooling, generally yields a deposit, consisting of yellow crystalline needles of purpurin mixed with amorphous particles of an alumina-compound, as may easily be seen by treating the deposit, after filtration, with boiling alcohol, which dissolves the purpurin with a yellow colour, leaving the alumina-lake undissolved as a dark-red powder. The solution, doubtless, contains purpurin in combination with alumina, for, on agitation with ether, it remains quite unchanged, whereas, after the addition to it of hydrochloric acid, ether takes up purpurin, forming a yellow solution, and leaving the liquid below only slightly coloured. Nevertheless, the combination is a very loose one, for if alcohol be added to the solution, to precipitate the excess of alum present, and the filtrate be evaporated, a mixture of alum crystals and needles of purpurin is obtained, from which the purpurin may be extracted by treatment with absolute alcohol, in which it dissolves with a yellow colour, an almost colourless crystalline mass being left. The solution in alum-liquor, when mixed with a little sodium carbonate or ammonia, the liquid still retaining an acid reaction, gives a flocculent precipitate, having the pink colour peculiar to the so-called madder lakes, which, as Robiquet long ago showed, are essentially compounds of purpurin with alumina. The precipitate is quite insoluble in a strong boiling solution of sodium carbonate, but dissolves easily in sodium hydrate.

An alcoholic solution of purpurin gives, with lead acetate, a dark crimson precipitate, which, on treatment with an excess of alcoholic lead acetate solution, dissolves, yielding a fine crimson solution. This solution shows three bands of absorption. This behaviour is characteristic, and may serve to distinguish purpurin from alizarin, which gives a lead-compound quite insoluble in alcoholic lead acetate.

An alcoholic solution of purpurin gives, with copper acetate, a dark reddish-yellow precipitate, whereas an alcoholic solution of alizarin becomes purple on the addition of copper acetate, and gives no precipitate, provided the alizarin is quite pure.

The derivatives of purpurin cannot be obtained with the same ease as those of alizarin and its isomerides. On endeavouring, for instance, to prepare methylpurpurin or ethylpurpurin, the difficulties encountered in consequence of the formation of various by-products are so great as to render the purification of the product almost impossible when only moderate quantities of material are taken. Schützenberger and Schiffert (*Traité des matières colorantes*, ii, 129) have described an ethyl-purpurin, but the composition given by them leaves it doubtful whether the compound contains one, two, or three molecules of ethyl.

Triacetylpurpurin.

This compound, first described by Liebermann and Giesel (*Deut. Chem. Ges. Ber.*, ix, 332), was prepared by heating purpurin with acetic anhydride at 180°. When heated, it begins to soften at 193°, and melts completely at 198—200°, which is somewhat higher than the temperature given by Liebermann and Giesel. It is decomposed even in the cold by dilute caustic potash lye, yielding purpurin. It is dissolved by concentrated nitric acid, giving a yellowish-brown solution, which, on the addition of water, deposits yellow flocks. These flocks dissolve in caustic potash lye, giving a fine pink solution which shows the absorption-bands of purpurin.

On analysis, the following results were obtained :—

0.3546 grm. of substance dried at 110°, gave 0.8154 grm. CO₂ and 0.1218 grm. H₂O, corresponding in 100 parts to

C	62.71
H	3.81

The formula C₁₄H₅(C₂H₃O)₃O₈ requires

C	62.82
H	3.66

Bromopurpurin.

When purpurin is digested with carbon disulphide containing bromine, hydrobromic acid is immediately evolved. Unless the temperature is raised to 150—200°, however, a portion of the purpurin remains unattacked. The product crystallises from glacial acetic acid in dark red lustrous needles, melting at 276°. Its properties are very similar to those of purpurin. It is, however, less soluble in

alcohol and glacial acetic acid than purpurin, and on being heated sublimes, leaving hardly any residue. In order to ascertain its composition, the amount of bromine contained in it was determined, the following results being obtained:

I. 0.1738 grm. of substance gave 0.0950 grm. AgBr, corresponding to 23.26 p.c. of bromine.

II. 0.2500 grm. of substance gave 0.1374 grm. AgBr, corresponding to 23.38 p.c. of bromine.

The formula $C_{14}H_7BrO_5$ requires 23.88 p.c. of bromine.

The product is, therefore, monobromopurpurin. This fact is of some interest, since it shows that purpurin differs from its isomerides in its behaviour to bromine. Anthrapurpurin, according to Perkin, takes up 2 atoms of bromine, while flavopurpurin, as we have recently ascertained, yields a product containing 3 atoms.

5. Action of Heat on Purpurin.

According to Schiel (*Ann. Chem. Pharm.*, lx, 76), purpurin, when strongly heated, undergoes some peculiar change, since the sublimate which is obtained no longer gives a red solution with caustic alkaline lye like purpurin, but dissolves with a violet colour. Bolley (*Journ. f. prakt. Chem.*, xcix, 305), maintains that at a temperature of 210—220°, purpurin is partly converted into alizarin. Quite recently, however, Rosenstiehl (*Compt. rend.*, lxxix, 669) has asserted that the observations of the chemists just named are erroneous.

Having heated some purified commercial purpurin in sealed tubes at 300° for several hours, we found that the purpurin had been entirely decomposed, yielding a carbonised mass, though no pressure from evolved gas could be observed on opening the tubes. On treating a small quantity of the product with caustic alkali, we obtained a violet solution which showed absorption-bands having the same position as those of alizarin, but a little broader than the latter. We now treated the whole contents of the tubes with boiling alcohol, and added to the filtered liquid an alcoholic solution of lead acetate. This gave a precipitate of lead alizarate, leaving in solution a lead-compound of quinizarin. As it was possible that the alizarin and quinizarin which we found had not been formed from the purpurin, but pre-existed in the specimen employed, the purpurin being simply decomposed by the heat applied, while the two other substances were left intact, we examined the purpurin we had taken by the method described in a previous note. This method is applicable to mixtures of purpurin and quinizarin, since the latter, like alizarin, remains unchanged when its alkaline solutions are exposed to the air. Now, our material was, indeed, found to contain small quantities of alizarin,

but not a trace of quinizarin. We therefore repeated our experiment by heating perfectly pure purpurin in sealed tubes as before. The product was quite free from alizarin, but contained quinizarin, which we, therefore, concluded is really a product of the action of heat on purpurin.

The quinizarin produced in this way has all the properties ascribed to the substance by its discoverer, Grimm (*Deut. Chem. Ges. Ber.*, vi, 508). It crystallises in bright red needles, melting at 193–194°. Its ethereal solution is strongly fluorescent, and shows two well-defined absorption-bands. Its alkaline solution is violet, like that of alizarin, and shows, like the latter, two absorption-bands, situated, however, somewhat further away from the red end of the spectrum. It is soluble in alum-liquor, giving a red solution which resembles that of purpurin in alum, and, like the latter, shows two absorption-bands.

In conducting the process of decomposition, whereby quinizarin is formed, it is advisable to discontinue heating before the purpurin is completely decomposed. The tube containing the latter having been heated at 300° during 6 or 7 hours, the contents are removed and treated with a boiling dilute solution of sodic carbonate, which dissolves a great part of the undecomposed purpurin along with various by-products. The residue is now treated with dilute caustic potash-lye, and the quinizarin and purpurin in solution are separated by the method described by Auerbach for purifying alizarin, i.e., by passing through it a current of carbonic anhydride as long as any precipitate is formed. The precipitate contains quinizarin with a little purpurin, the latter being, for the most part, left in solution. The precipitate is filtered off and treated with hydrochloric acid, and the flocks left by the acid are again dissolved in caustic lye, carbonic anhydride being a second time passed through the solution. The process is repeated until the filtrate no longer contains purpurin.

The yield of quinizarin is but trifling, and is surpassed by that of the by-products formed at the same time. The latter cannot be obtained in a form suitable for analysis, and we are, therefore, unable to give any explanation of the cause of this remarkable metamorphosis.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Spectroscopic Reactions of Magnesium Salts. By F. VON LUTPPEL (*Deut. Chem. Ges. Ber.*, ix, 1845—1849).—This communication relates to the modification of the spectrum of purpurin when in combination with magnesia. Reference must be made to the diagram given in the original paper, in order to understand the modification which the spectrum of purpurin undergoes. Purpurin alone dissolved in water gives two absorption-bands, one between the lines D and E, but nearer E than D, and one between b and F, nearer F than b. In presence of magnesium chloride, these bands are intensified. With alum, the band between E and E removes to nearer D; and with calcium chloride, the absorption-bands are greatly extended. Acetic acid destroys the influence of magnesium chloride, but not of alum. Calcium chloride and alcohol give precisely the same spectrum as magnesium salts. It is necessary, therefore, to precipitate the salts of the alkaline earths with a neutral tartrate, before testing for magnesia. W. R.

Fluorescence. By E. LOMMEL (*Pogg. Ann.*, clix, 514—536).—The results of the author's experiments are summed up in the following statements:—

There are two kinds of fluorescence. In the first kind, each exciting homogeneous ray, the refrangibility of which falls within the limits of the fluorescence spectrum, or within a certain region of it, develops not merely rays of equal or greater wave-length than itself, but also rays of shorter wave-length. In the second kind, each exciting homogeneous ray develops only those rays of the fluorescence spectrum which possess a greater or less similarity to itself in wave-length.

To some bodies only the first kind of fluorescence belongs, each exciting homogeneous ray developing the entire fluorescence spectrum. Such bodies are, therefore, not amenable to the law of Stokes. Naphthalene-red, chlorophyll, and eosin belong to this class.

Other substances display the second kind of fluorescence only, and, therefore, follow the law of Stokes throughout the entire extent of their fluorescent spectrum. To this class belong the majority of fluorescent substances which have hitherto been examined.

There exists a third class of substances which exhibit both kinds of fluorescence; a certain region of their fluorescence spectrum belongs to the first kind, while the remainder possesses the second kind of fluorescence. These bodies, of which chameleon-red, chameleon-blue, and chameleon-green are examples, only in part conform to Stokes's R. R.

Division of the Positive Metal in the Galvanic Circuit between Two Acids. By F. FUCHS (*Pogg. Ann.*, cliv, 486—489).—When two similar Daniell piles are opposed, each containing in its exciting liquid the same amount of sulphuric acid in equal volumes, but one having, in addition, a quantity of acetic acid in the liquid, that pile which contains the acetic acid shows a potential difference somewhat less than that of the other. This proves that the zinc in the cells containing the mixture is divided between the two acids.

R. R.

The Movements of Electrified Mercury. By H. HERWIG (*Pogg. Ann.*, cliv, 489—492).—A drop of mercury, placed on a glass plate and strongly electrified by the pole of a Holtz machine, becomes flattened, and the capillary depression of mercury in a narrow glass tube is greatly diminished. These effects are much more marked when the positive pole of the machine is used than when the negative pole is used, and the difference is probably due to the higher tension which the electricity of the positive pole of the Holtz machine has been observed to possess.

R. R.

Nobili's Rings on Gold. By J. SCHIEL (*Pogg. Ann.*, cliv, 493—496).—A plate of burnished pure gold was immersed in water acidulated with nitric acid, and made the positive pole of battery, the other pole being the extremity of a platinum wire, placed a short distance above the gold plate. After the current had passed for 10 minutes, the gold was removed, washed, and dried. On its surface there now appeared somewhat pale concentric rings, but after exposure to direct sunlight for a few hours, the rings became brilliantly coloured. When an alkaline, instead of an acid, electrolyte was made use of, the same effects were produced, but less powerfully.

R. R.

Dependence of the Electric Conductivity of Selenium on Heat and Light. By W. SIEMENS (*Pogg. Ann.*, cliv, 117—141).—With no substance other than selenium did the author succeed in detecting any effect of light in changing the conductivity. This effect being therefore a property special to selenium, and not a general action of light, its explanation must be sought for in some exceptional characteristics of the element.

When amorphous selenium is gradually heated, the remarkable thermal phenomena observed by Hittorf occur, and these are accompanied by notable variations in the conducting power. Up to the temperature of 80° no conductivity was manifested; at 162° a current passed measured by 870 scale-divisions of the reflecting galvanometer; this conductivity diminished as the temperature rose to 217°, the melting point, when the instrument marked 70 divisions; and as the heating was continued above the melting point, the conductivity again rose until a galvanometer-reading was reached of 300.

When amorphous selenium is kept for some time at the temperature of 210°, its physical properties are so completely changed, that the electric conductivity is 50 times greater than that of the crys-

talline modification which is obtained by heating selenium to 150° ; and while the conductivity of this last modification increases as the temperature rises, that of the former diminishes, its behaviour in this respect resembling that of metals. A number of other observations on variations of the conductivity of selenium by allotropic changes, electric currents, temperature, &c., under conditions which cannot be easily defined in a brief abstract, are recorded in the paper.

The author's experiments on the effect of light in augmenting the conductivity of selenium, seem to show that a surface action is concerned. When to one side of a thin plate of selenium a pole, formed of a grating of 20 platinum wires, was applied, and to the other side a pole formed of a grating of 10 similar wires twice as far apart, the conductivity under the influence of light was twice as great when the positive pole of the battery was connected with the 10 wire grating, as it was in the opposite case.

R. R.

Electrolysis with Evolution of Hydrogen at both Poles. By EMIL ELSÄSSER (*Deut. Chem. Ges. Ber.*, ix, 1818, 1821).—When a current is passed through a voltameter, the anode of which consists of magnesium and the liquid either of dilute sulphuric acid, or of magnesium sulphate solution, hydrogen is evolved at both poles. In the latter case, magnesium hydrate is deposited. Experiments show that the amount of hydrogen evolved at the anode is exactly half that evolved at the cathode; and that the weight of magnesium, partly dissolved and partly precipitated as oxide at the anode, correspond exactly:—the dissolved portion with the salts thrown off at the cathode, and the hydrogen evolved in a voltameter included in the circuit; the precipitated portion with the hydrogen evolved at the anode itself. Experiments with zinc and aluminium gave no results of value, although Wöhler and Buff (*Ann. Chim. Pharm.*, ciii, 218) obtained with the latter metal similar results to the above.

The appearance of hydrogen at both poles may be ascribed to the affinity of magnesium for oxygen, which induces it to take up an amount from the water in addition to that liberated on the surface of the plate. But the relation between the quantity of the oxygen taken up, to the hydrogen evolved at the cathode, is not as yet accounted for.

C. L. F.

The Specific Heat of Mercury. By A. WINKELMANN (*Pogg. Ann.*, clix, 152—165).—This paper describes in detail three series of experiments, giving very concordant results, and leading to the unexpected conclusion that the specific heat of mercury is somewhat less at higher than at lower temperatures. According to the author's results, the specific heat of mercury, C , at the temperature t° , is expressed by the formula—

$$C_t = C_0 + at$$

where $C_0 = 0.03336$, and $a = -0.0000069$.

R. R.

Thermal Changes accompanying the Solution of Ammonium Nitrate in Water. By TOLLINGER (*Chem. Centr.*, 1876, 530).—

1. 1 molecule salt is mixed with (<i>m</i>).	2. 1 gram salt is mixed with (<i>P</i>).	3. Absorbed for molecule. (Thermal units) (<i>W</i>).	4. The tem- perature of the solution sinks to (<i>σ</i>).	5. The solution is saturated at (<i>L</i>).	6. Cooling value of the solution per gram of salt for the temperature <i>L</i> , when the initial temperature of the materials was =			
					20°.	15°.	10°.	5°.
3·85 mols. H ₂ O.	0·75 gram H ₂ O.	3975 T. V.	44·7° C.	+ 5° C.	33·0 T.V.	38 T.V.	44·1 T.V.	49·7 T.V.
3·79	0·85	4083	42·2	0	26·8	32·9	38·9	45·0
3·98	0·90	4127	41·3	2	24·1	30·3	36·6	42·8
4·18	0·94	4172	40·3	4	21·1	27·5	34·0	40·5
4·39	0·99	4217	39·3	6	17·8	24·5	31·2	37·9
4·61	1·04	4264	38·3	8	14·4	21·3	28·3	35·3
4·84	1·09	4311	37·4	10	10·6	17·8	25·1	32·3
5·08	1·14	4358	36·4	12	6·7	14·1	21·6	29·1
5·34	1·20	4408	35·5	14	2·3	10·1	17·9	25·7
5·61	1·26	4457	34·6	16		5·7	13·8	21·9
5·82	1·31	4494	33·9	17·5		2·3	10·6	18·9
6·03	1·49	4629	31·5	16		0·9	10·1	19·3
7·98	1·80	4825	28·3	14			9·1	29·8
9·77	2·20	5041	26·0	12			9·7	21·8
12·26	2·76	5281	22·1	10			6·5	21·4
16·03	3·61	5524	18·1	8			0·4	19·4
100·00	5·03	5863	14·0	6				15·8
200·00	7·82	6216	9·7	4				5·4
22·84	16·57	6625	5·0	2				
34·99	22·50	6788	3·7	1·5				
73·64	45·00	6907	1·9	0·8				

The table on page 679 affords the means of calculating the quantities of ammonium nitrate and water which must be employed in order to freeze a definite quantity of any liquid.

Let Q represent the amount of heat to be withdrawn; column 2 (p) gives the proportion in which the salt and water must be mixed in order to attain the required final temperature I (5), and column 6 (q) the available cold per gram of salt. $\frac{Q}{q}$ then represents the amount of salt to be used, and $p \frac{Q}{p}$ the amount of water.

Generally $Q = Pc(t - I)$ if P be the weight of substance to be cooled, c the thermal capacity, t , the initial and I the final temperature.

In practice the following points must be considered: 1. The water-value of the vessels. 2. Loss of cold. 3. The fact that the last quantities of the salt dissolve very slowly in the already nearly saturated solution.

M. M. P. M.

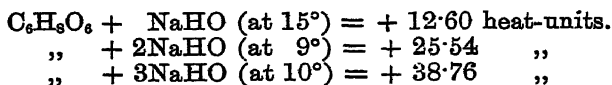
The Temperatures of Combustion. By M. BERTHELOT (*Compt. rend.*, lxxxiv, 407—412).—From hypothetical and experimental data, the author deduces an algebraical formula for the temperature of the combustion of a gas in presence of a given excess of oxygen or of an inert gas. He proves that the temperature of combustion of carbonic oxide by oxygen at constant volume must lie between 2,600° and 4,000°; by air between 1,750° and 2,200°; that of hydrogen by oxygen between 2,400° and 3,800°; by air between 1,750° and 2,100°.

R. R.

A New and Accurate Method for Determining Boiling-points with Small Quantities of Liquid. By P. T. MAIN (*Chem. News*, xxxv, 59).—The apparatus for determining boiling-points at a standard pressure consists of a V-shaped narrow glass tube, having the shorter limb (2 in.) hermetically sealed, and the other limb (18 in. long) connected by means of a drying tube with a long vertical glass tube, which dips into water contained in a wider tube, so that by raising or lowering the wider tube the pressure inside the boiling-tube may be made greater or less than that of the atmosphere. The liquid to be operated on is poured into the V-tube, and in such quantity that by inclining the tube the air in the shorter limb may be displaced, the liquid occupying it and a portion of the longer limb. The heat is applied by means of hot water, or of a solution of high boiling-point if the liquid boil higher than 100°, and the pressure is applied by aid of the pressure-tube, so as to make it exactly equal to 760 mm. By regulating the temperature so that the levels of the liquid in both limbs are equal, it is possible to determine the boiling-point of only 1 c.c. of liquid. The results of several experiments are given, showing, by the closeness with which they agree with one another, the degree of accuracy.

E. W. P.

Thermochemical Researches upon Citric Acid. By BERTHELOT and LOUGUININE (*Compt. rend.*, lxxxi, 909; *Chem. Centr.*, 1876, 9).—Combinations were made of citric acid with alkalis and alkaline earths in varying proportions. The conclusions are: 1. If three equivalents of soda be successively added to 1 molecule of citric acid (192 grams dissolved in 6 litres), the quantity of heat evolved is almost the same after each addition. The numbers were—



2. In presence of much water, no further evolution of heat occurs on adding a quantity of soda in excess of that required for the formation of the tribasic salt: in concentrated solutions a slight evolution of heat does however occur.

This is to be accounted for by remembering that citric acid is tetrameric, although only tribasic.

We may imagine the fourth hydroxyl group replaced by soda, when the solution is concentrated, the compound being decomposed by excess of water.

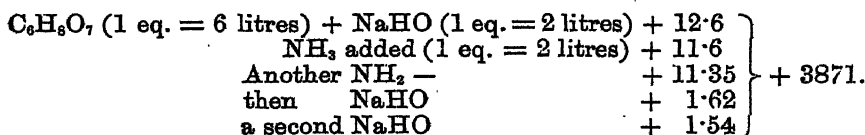
3. One molecule of citric acid when mixed with 3 mols. of soda, evolves almost three times as much heat as is evolved by 1 mol. of acetic acid (3×12.9 in place of 13.3).

The action of water upon various citrates is then examined. When the tribasic sodium salt is mixed with large volumes of water, a very slight absorption of heat only takes place: this salt is therefore stable.

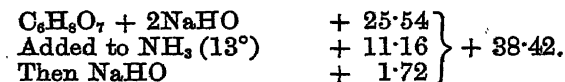
The heat evolved by the action of 1, 2, and 3 mols. of ammonia in citric acid was 11.19, 22.44, and 33.99 units respectively: these numbers are not much less than those obtained with soda. The addition of two additional mols. of ammonia caused scarcely any sensible evolution of heat.

With baryta the following numbers were obtained: 1 mol. + 13.37 (no ppt.); 2 mols. + 27.7 (ppt.); 3 mols. + 42.72 (ppt.); 4 mols. + 0.69.

The action of two distinct bases upon citric acid was examined—



Disodium citrate and ammonia—



The molecule of citric acid takes up successively the different bases to form soluble double salts. Ammonia in citrate is completely displaced by soda. The sum of the heat evolutions in the foregoing instances is almost equal to the heat evolution in the formation of

tribasic sodium citrate, viz., 38.76. The action of hydrochloric, nitric, and acetic acid upon citrates is then considered—

	Calculated.
$C_6H_5Na_3O_7$ (1 eq. = 6 litres) + $\frac{1}{2}HCl$ (1 eq. = 2 litres) =	+ 0.24 0.48
+ $1HCl$	= + 0.59 0.92
+ $3HCl$	= + 3.08 3.21
+ $6HCl$	= + 3.25 3.21

M. M. P. M.

Apparatus for Fractional Distillation in a Vacuum. By W. THÖRNER (*Deut. Chem. Ges. Ber.*, ix, 1868—1870).—This apparatus differs from an ordinary fractionating bulb, condensers and receiver, by having a glass bulb with three tubulars introduced between the condenser and the receiver. Through one of these tubulars, the tube of the condenser passes; through another, the air is exhausted; while the third, communicating with the receiver, is provided with a stopcock which may be closed while the receiver is being changed.

W. R.

Simple Exhausting and Compressing Air Pump. By C. BULK (*Deut. Chem. Ges. Ber.*, ix, 1871—1872).—This apparatus consists of a Woulff's bottle with three necks, through one of which is inserted an injector, through another a tube for leading off the air, while the third serves as an overflow pipe for the water, the pressure naturally depending on the length of the tube. The injector cannot be described without referring to the annexed diagram.

Note by Abstractor.—A very simple injector capable of giving an exhaust of 400 millimeters may be constructed out of a broken test-tube, four inches long; a T-piece is sealed on about an inch from its upper extremity; both of the test-tube ends are closed with perforated india-rubber corks, through the upper of which a tube drawn out to a moderately fine point passes, and is inserted loosely into the end of another, which serves to carry off the water. The air passes into the test-tube through the T-piece. It is advisable to make the exit-tube sinuous, a much better suction being thereby obtained. The apparatus can be made and fitted up in a quarter of an hour. W. R.

Construction of Scientific Instruments of Rock Crystal. By S. STEIN (*Deut. Chem. Ges. Ber.*, ix, 1824—1826).—The author points out the advantages attending the employment of rock crystal for balance beams and pans, and measuring instruments. The great advantage being the very small degree to which such instruments are affected by changes of temperature or other influences, by which aluminium would be seriously impaired. The specific gravity of rock crystal is nearly that of aluminium.

Thermometers have been made with great success of the same material. The capillary tube is bored out with a fine steel drill, and the bulb likewise.

They are closed with ground quartz stoppers, which are held in tightly by the pressure of the air. Such thermometers are very constant.

C. L. F.

Use of the Magic Lantern for Chemical Demonstrations. By H. LANDOLT (*Deut. Chem. Ges. Ber.*, ix, 1849—1857).—This apparatus is used by the author for throwing the images of small retorts, flasks, &c., in which operations are being conducted, on a screen, so that they appear more than six feet in diameter. The lantern is permanently fixed at the left hand of the audience, and the screen on which the apparatus is exhibited on the right hand. The frame on which the lantern rests is provided with a wooden shelf, 125 c.m. long, and 54 c.m. broad, which may be turned horizontally on an axis, and may also be slightly inclined upwards, so as to secure that the image appears on the middle of the screen. A Drummond light is used for the lantern, the lenses being a pair of convex lenses, of 7 c.m. focus and 8 c.m. aperture, in order to concentrate the light on the glass apparatus, which are placed about 15 c.m. from the lantern. Enough room to conduct operations is thus secured. The light then passes through a convex lens of 17 c.m. focus, and another of 60 c.m., both having 11 c.m. apertures. Each of these lenses is fixed on a separate stand, so that they may be conveniently moved. The tiny apparatus was constructed by Geissler, and must not occupy more room than a circle 8 c.m. diameter. The author remarks that the spectators soon become accustomed to seeing all the apparatus inverted, but this inconvenience is easily remedied, though at the expense of brilliancy, by reflecting the rays from the first lens from a crown glass prism.

The solidity of the apparatus prevents every portion from being distinctly seen at once; it is advisable for the most part to focus the edge of the apparatus, or the divisions of a graduated tube. Among other experiments which may be thus shown, are: 1st. Decomposition of water in a graduated U-tube 40 mm. long and 15 mm. wide; 2nd. Absorption of hydrogen by palladium; 3rd. Eudiometric experiments in a small Hofmann's U-tube, each limb of which is 53 mm. long, and 13 mm. wide; complete disappearance of oxygen and hydrogen in the proportion of 1:2; explosion of 2 vols. of carbon monoxide with 1 vol. of oxygen; decomposition of ammonia gas by the electric discharge; this experiment is over in a minute, owing to the small amount of the gas to be decomposed; 4th. Absorption of gases, *e.g.*, ammonia or hydrochloric acid, and mixture of nitric oxide with oxygen; 5th. Liquefaction of gases; 6th. Coloured vapours, manufacture of sulphuric acid, preparation of bromine, chromium oxychloride, &c.; 7th. Coloured liquids; 8th. Crystallisation, and electrolytic decomposition of salts; and, 9th, the apparatus may also be used for exhibiting photographs of apparatus used in industrial operations.

W. R.

Inorganic Chemistry.

New Method of preparing Phosphoric Acid. By G. F. H. MARKOE (*Proc. Americ. Pharm. Assoc.*, 1875; *Arch. Pharm.* [3], ix, 531—539).—By the following method, large quantities of phosphoric

acid can be prepared with less danger and much more quickly than by any other method hitherto known. 1 part of phosphorus, 6 parts of nitric acid (sp. gr. 1.42), 1 part of water, and a sufficient quantity of bromine or hydrobromic acid, are the substances required. After the phosphorus has been mixed with the acid in a bottle large enough to hold twice the contents of the total substances used, a glass funnel is fixed to the neck of the bottle, and the funnel covered with a smaller one. A few drops of bromine or hydrobromic acid are then introduced into the bottle, the latter being kept cold by placing it in cold water. As soon as the reaction ceases, the bottle is taken out of the water and heated. It is best to add a few granules of iodine to the mixture.

What the author claims to be new in this method is the use of bromine or iodine, or both, in conjunction with phosphorus and nitric acid. The following equation explains the reaction that takes place, $PBr_3 + 4H_2O = H_3PO_4 + 5BrH$; the hydrobromic acid formed is at once decomposed by the nitric acid, liberating bromine, and forming nitric oxide and water; thus, $6BrH + 2HNO_3 = 6Br + 4H_2O + 2NO$. The bromine set free again acts on a fresh quantity of phosphorus, and the above-mentioned reaction repeated. From this it is seen that a small quantity of bromine, when used continually, suffices to convert a very large amount of phosphorus into phosphoric acid. After the phosphorus has been dissolved completely, the contents of the bottle are transferred to a porcelain dish, and the excess of nitric acid is expelled by evaporating the liquid to a syrup. The latter is treated with water, and the resulting phosphoric acid solution made up to its required strength. The author uses a solution containing 50 p. c. of H_3PO_4 .

When iodine is added besides bromine, better results are obtained, owing probably to the formation of iodine bromide, which is soluble in water. Iodine and phosphorus form a triiodide, which is decomposed by water into hydriodic and phosphorous acids. The small quantities of iodine or bromine remaining in the liquid after the end of the reaction are volatilized when the excess of nitric acid is driven off. When concentrated nitric acid is used, it is necessary to keep the mixture quite cold, for which purpose it is advisable to place the mixture in ice; bromine can then be added in much larger quantities without danger of explosion. To render the process quite safe, the author first adds the bromine and iodine to the phosphorus in the water, and then the acid. It may also be mentioned that very large quantities of phosphorus require but little more bromine or iodine than one or two ounces of phosphorus. When hydrobromic acid is used instead of bromine, the whole of the former can be added to the mixture in one operation.

As the trichloride and pentachloride of phosphorus are decomposed by water, the former yielding phosphorous acid, and the latter forming phosphoric acid, it was thought that phosphoric acid might be prepared by dissolving phosphorus in nitro-hydrochloric acid, which contains free chlorine, and that the latter might produce these compounds. Experiments with this view were accordingly undertaken with aqua regia, but the results were very unsatisfactory. A small

quantity of bromine or iodine when added gave results which were identical with those above mentioned.

For making small quantities of phosphoric acid the following method may be recommended. The apparatus used is similar to the one already described; 2 ounces of phosphorus are put into the bottle with 12 ounces of water, and 10 grains of iodine, then 40—60 grains of bromine are added drop by drop. When the reaction ceases, 12 ounces of nitric acid (sp. gr. 1.42) are added, and the bottle and contents placed in a water-bath. The bottle must be placed so that the liquid within it may be on the same level as the water outside it.

If after the lapse of 24 hours, complete solution of the phosphorus has not taken place, the bottle with its contents may be warmed slightly. After this, the solution is poured into a porcelain dish and heated in order to expel the excess of nitric acid, bromine, and iodine, a temperature of about 400° F. being required. The resulting acid is diluted to a specific gravity of 1.350, equal to 50 p.c. of H_3PO_4 .

In conclusion, the author mentions that in all samples of phosphorus which were obtained from the New Jersey works arsenic was found, often to the extent of 0.6 gr. of arsenious acid in 4 kilos. of phosphorus, and that for pharmaceutical purposes the arsenic should always be separated by means of sulphuretted hydrogen. It is further stated that it is not altogether necessary to use pure nitric acid of 1.42 sp. gr. for the above mentioned methods, more dilute acid, if added in adequate quantities, effecting the purpose equally well. D: B.

Phosphorus Oxychloride. By IRA REMSEN (*Deut. Chem. Ges. Ber.*, 1872—1876).—The author formerly ascertained that carbon monoxide is very slowly oxidised by ozone. On trying the action of ozone on another unsaturated compound, viz., phosphorous chloride, phosphorus oxychloride was formed. This makes it probable that the oxychloride, sulphochloride, and pentachloride have analogous constitutions: this hypothesis is also supported by the specific volume of phosphorus in the three compounds, and by their dissociation when in the state of vapour. W. R.

Preparation of Alkaline Nitrites. By A. ÉTARD (*Compt. rend.*, lxxiv, 234).—Equal molecules of nitrate and sulphite of potassium or sodium are fused together in a crucible at a red heat. The sulphite oxidises at the expense of the nitrate, and the latter is reduced to nitrite. The fused mass is powdered and boiled with alcohol, which takes up the alkaline nitrite, but does not dissolve the sulphate. In this way large quantities of pure potassium or sodium nitrite can be easily prepared. J. W.

Cæsium and Rubidium Compounds. By R. GODEFFROY (*Arch. Pharm.* [3], ix, 343—347).—*Cæcio-platinous chloride*, $PtCl_2 \cdot 2CsCl$, forms long monoclinic prisms, which appear dark red by transmitted light, but yellowish-green and highly lustrous as prepared by the process described below. The crystals are unaltered in air: they fuse when heated, but are not decomposed. At a red heat chlorine is given off; the residue contains cæsium chloride mixed with

metallic platinum. 100 parts of water dissolve the following quantities of the salt:—

20°.	40°.	60°.	80°.	100°.
3.4	6.73	8.68	10.92	12.10 parts.

The aqueous solution is dark yellowish-red: it is not changed on boiling: if alcohol be added to the boiling solution, metallic platinum is thrown down. The same decomposition is brought about more rapidly and more completely by boiling the aqueous solution with glycerin. The salt is produced by heating cæσιο-platinic chloride with pure oxalic acid to fusion in a platinum crucible, or by passing hydrogen over the double chloride in a state of fusion, treating the residue with boiling water, filtering from metallic platinum, evaporating and crystallising. The crystals are washed with a little cold water, and then with alcohol, and are dried at 100°.

Cæsium chloride, CsCl, does not crystallise in the regular system: it forms rhombohedra with rounded edges.

Rubidium chloride, RbCl, crystallises in the regular form: $\infty O \infty$ predominates.

Rubidio-antimonous chloride, $SbCl_3.6RbCl$, forms hexagonal tables of the combination OP.P. Exact measurements of P could not be obtained. The ratio of subsidiary to main axes is 1 : 1.836.

Rubidio-ferric chloride, $Fe_2Cl_3.6RbCl$, is produced as small yellowish-red monoclinic crystals by evaporating mixed solutions of ferric and rubidium chlorides with a little hydrochloric acid. The crystals are not deliquescent, nor are they altered by exposure to air. $\infty P = 132^\circ$. $\infty P \infty (\infty P : \infty \bar{P} \infty) = 118^\circ 30'$. $\bar{P} = \infty = 72^\circ$ in axis C: $mP \infty = 71^\circ 20'$ in axis C. Axis relation $a : b : c$ is about 0.59 : 1 : 0.82. The salt is easily soluble in water, but is insoluble in alcohol and in ether. The aqueous solution is partially decomposed on boiling.

Cæσιο-palladious chloride is produced in the form of a yellow crystalline precipitate by mixing a solution of cæsium chloride with a solution of palladious chloride. By boiling with water the salt is decomposed, the whole of the palladium being precipitated in the metallic form.

M. M. P. M.

Ultramarine. By W. STEIN (*J. pr. Chem.* [2], xiv, 387—397).—The author's experiments lead to the conclusion that the sulphur in ultramarine, in so far as it is not in combination with oxygen, is present as aluminium sulphide; and that the colour of ultramarine depends on the proportion of aluminium sulphide which it contains. It is also stated that ultramarine is easily decomposed by boiling with a solution of copper sulphate.

G. T. A.

Constitution of Ultramarine. By J. PHILIPP (*Liebig's Annalen*, cxxxiv, 132—162).—Blue and green ultramarines were carefully analysed. Methods are detailed whereby the sulphur obtained from H_2SO_4 , that from H_2S and SO_2 , that from SO_3 and SO_2 , and that from H_2S and polysulphides, was determined. It was found, however, that the reactions which ensued among the various sulphur compounds

when these were set free during the process of analysis, were too complicated to allow of trustworthy determinations being made of the absolute quantities of sulphuretted hydrogen and of the oxycompounds of sulphur existing in the ultramarine. These oxycompounds of sulphur are not removed from ultramarine by heating with water to a temperature of 200° . The facts that blue ultramarine may be obtained from green without altering the composition, so far as these sulphur compounds are concerned, and that metallic derivatives of ultramarine may be produced, which, although containing the same sulphur compounds, are nevertheless not true ultramarines at all, show that the constitution of the blue variety of ultramarine is not dependent upon the presence of oxycompounds of sulphur. Green ultramarine may be changed into blue (1) by heating with iodine in presence of air; (2), by heating with iodine solution to 140° or 160° , at higher temperatures complete decomposition ensues; (3) by fusion with boric acid, or by repeated evaporation with a solution of boric acid; (4) by heating with water to 160° ; (5) by continued boiling with solutions of the following salts:—zinc sulphate, mercuric chloride, nickel sulphate, cadmium sulphate, manganese sulphate. These reactions are most readily explained by supposing that sodium sulphide is withdrawn from the green ultramarine. It is shown that when green ultramarine is converted into blue by heating with water, almost no alteration in weight occurs, and that the amounts of the various sulphurs (see above) is exactly the same in blue ultramarine as in the green from which the blue was produced. It is evident therefore that the difference between the green and blue varieties cannot be ascribed to oxidation of the sulphur in the latter; it is much more probably due to traces of sodium sulphide present in the green variety. Blue ultramarine fused with a mixture of sodium sulphate, and a little charcoal was converted into the green variety. The paper concludes with the results of experiments, which are not yet completed, on the action of various metallic salts upon blue ultramarine. In most cases the ultramarine was completely decomposed. The reaction of silver nitrate seems to result in the formation of a true silver ultramarine. M. M. P. M.

Irisation of Glass. By E. FREMY and CLÉMANDOT (*Compt. rend.*, lxxxiv, 209, 210).—Glass submitted to influences which very slowly effect its decomposition, such as exposure to continued moisture; to exhalations arising from damp earth; to ammoniacal or acid vapours; often becomes covered with a thin film or scale, which produces very remarkable phenomena of irisation. The authors have, after many experiments, succeeded in imitating this effect, and have produced glass with an adherent coating, resembling nacre or mother-o'-pearl, by submitting the glass, under the influence of heat and pressure, to the action of water containing 15 per cent. of hydrochloric acid. The conditions necessary to ensure success, the composition of the external film, the alterations produced in it by different chemical reagents, &c., will be described in a subsequent communication. They are of opinion that the facility with which glass undergoes irisation, that is to say, the facility with which it is attacked, should be studied by those who

manufacture glass for special objects, and they suggest that such glass should be qualitatively examined in the manner above mentioned.

J. W.

The Oxide of Titanium obtained by the Solution of Titanium in Acids, and some New Titanium Compounds. By EMANUEL GLATZEL (*Deut. Chem. Ges. Ber.*, ix, 1829, 1839). The author, upon consideration of the following salts obtained by him from metallic titanium, comes to the conclusion that by dissolving titanium in sulphuric and hydrochloric acids, compounds of the titanium sesquioxide are formed; that hydrofluoric acid forms directly fluoride of titanium, and that in no case can protoxide compounds be formed by solution of the metal in acids.

Titanium Sesquichloride, $\text{Ti}_2\text{Cl}_6 + 8\text{H}_2\text{O}$, is obtained by dissolving titanium in hydrochloric acid; evaporation and filtration from deposited titanic acid. It is a green salt, forming with water an opalescent solution, due to separation of titanic acid, into which the whole gradually becomes converted. Analysis gave results leading to the formula, $\text{TiCl}_6 + 8\text{H}_2\text{O}$.

Sulphate of Titanium Sesquioxide.—Obtained by dissolving titanium in sulphuric acid, and evaporating down, when the violet salt crystallised out in small foliate groups of crystals. Their aqueous solution was clear, but after a time a black deposit settled, becoming white in time. Formula, $\text{Ti}_2\text{S}_2\text{O}_{12} + 8\text{H}_2\text{O}$.

Sulphate of Titanium Dioxide, $\text{TiS}_2\text{O}_8 + 3\text{H}_2\text{O}$, is a yellow resinous mass, obtained by the action of sulphuric acid on the solution of the above sulphate. It is very soluble in water, and absorbs moisture greedily from the air, becoming liquid. On heating it to redness, water and sulphuric acid are given off, and a white mass (probably titanic acid) is left behind.

Double Sulphate of Titanium Dioxide and Potash.— $\text{K}_2\text{SO}_4 \cdot \text{TiS}_2\text{O}_8 + 3\text{H}_2\text{O}$ forms small white crystals, obtained by treating potassium sulphate with the above, and crystallising in a vacuum over oil of vitriol.

Titanium Fluoride.—The action of hydrofluoric acid on metallic titanium gives a clear solution, from which ammonia precipitates titanic acid. The titanium therefore immediately passes from the sesquifluoride (probably formed at first) to the fluoride. No exact analytical results were obtained.

From the compounds formed by the action of sulphuric and hydrochloric acids on metallic titanium, the author inclines towards Rose's assertion, that titanic ironstones contain neither titanium protoxide nor titanic acid, but consist chiefly of titanium sesquioxide and iron oxide, for titanic ironstone dissolves in sulphuric acid to a blue solution, which resembles the sulphate of titanium sesquioxide in every respect. This is easily explained taking Rose's view of the case; whereas Moscoeder's theory to be correct, would necessitate the reduction of the titanic acid by the oxide of iron, which, by the equation, $2\text{FeO} \cdot 2\text{TiO}_2 = \text{Fe}_2\text{O}_3 + \text{Ti}_2\text{O}_3$, would form sesquioxide of titanium and ferric oxide. In the original solution exactly the converse takes place in course of time. The author assigns titanium with respect to the properties of binoxide, a place in the elements between tin and silicon,

but for its sesquioxide combinations, he places it with iron, chromium, manganese, and aluminium. For although sesquioxide compounds of silicon are known, it does not appear probable that such as contain water will ever be obtained. With tin the existence of any sesquioxide compound is problematical. In its behaviour to acids titanium resembles aluminium, both of these metals yielding sesquioxide compounds. The sulphate when heated yields an insoluble basic salt; so does the corresponding iron sulphate, while the salt Ti_2Cl_6 is analogous to the chloride of chromium, Cr_2Cl_6 . C. L. F.

Preparation of Earth-Metals. By E. FREY (*Liebig Annalen*, clxxxiii, 367, 368).—These metals are prepared in considerable quantities by Bunsen's electrolytic process, at the chemical manufactory of Dr. Schuchardt, at Carlitz, and specimens of barium, calcium, strontium, lithium, and cerium were sent to the exhibitions at Philadelphia and London. *Calcium* thus prepared entirely resembles aluminium in appearance, and is not yellow, as commonly described. It is brittle, and not ductile. *Strontium* is a bright brass-yellow, very malleable metal, easily rolled out into plates or drawn into wire; it oxidises more quickly than calcium. *Barium*, from its high fusing point, is difficult to obtain. *Cerium* prepared in this manner possesses all the properties of that which Wöhler obtained by reducing cerium chloride with metallic sodium. E. N.

Double Haloid Salts of Cadmium. By J. M. EDER (*Chem. Centr.*, 1876, 515).

	Solubility.			
	Water.	Alcohol. 0·794 sp. gr.	Ether. 0·729 sp. gr.	eq. vols. of alcohol and ether.
$2NH_4Br \cdot 2CdBr_2 \cdot H_2O$	0·73	5·3	280	24
$4NH_4Br \cdot CdBr_2$	0·96	decomposed.		
$2NaBr \cdot 2CdBr_2 \cdot 5H_2O$	1·04	3·7	190	—
$4KBr \cdot CdBr_2$	1·40	decomposed.		
$KBr \cdot CdBr_2 \cdot H_2O$	0·79	decomposed.		
$2NH_4I \cdot 2CdI_2 \cdot H_2O$	0·90	0·88	2·4	—
$2NH_4I \cdot CdI_2 \cdot 2H_2O$	0·58	0·70	8·9	1·8
$2NaI \cdot CdI_2 \cdot 6H_2O$	0·63	0·86	10·1	—
$KI \cdot CdI_2 \cdot H_2O$	0·94	—	—	—
$2KI \cdot CdI_2 \cdot 2H_2O$	0·73	1·4	24·5	4·5

M. M. P. M.

On Crystallised Dicalcium Phosphate. By MILLOT (*Chem. Centr.*, 1876, 611).—When calcium chloride, sodium phosphate, and sufficient acetic acid to dissolve the precipitate formed are heated together, dicalcium phosphate, $CaHPO_4 + 2aq.$, in the form of quadratic prisms, crystallises out. E. W. P.

Crystalline Phosphate and Arsenate of Copper and Zinc. By FRIEDEL and SARASIN (*Chem. Centr.*, 1876, 611).—This compound is obtained by heating in sealed tubes to 130—140°, a mixture of water, phosphoric and arsenic acids, together with copper and zinc phosphates. By this method libethenit, olivin and adamin were obtained. E. W. P.

Action of Water and Saline Solutions upon Lead. Parts II and III. By M. M. PATTISON MUIR (*Proc. Manch. Lit. and Phil. Soc.*, xvi, 1—10 and 141—152).—The results obtained in these parts of the author's investigations are mainly these:—

1. There is *generally* an increase in the solvent action of dilute saline solutions upon lead, associated with increase of exposed surface of liquid, when the experiments are carried out in beakers loosely covered with porous paper.

2. When very large surfaces of liquid are exposed, the increase in quantities of lead dissolved becomes extremely irregular. It would appear as if exposure of the liquid to large surfaces of air were less fitted to promote solvent action than exposure to smaller surfaces of air. This view is rendered more probable by the fact that when air was passed through flasks containing various liquids and pieces of lead, less lead passed into solution than when a moderately sized surface of liquid was simply exposed to the air. The action of the air results in the formation of an insoluble hydrocarbonate: in certain solutions this salt is more quickly formed than in others.

3. The solvent actions of those saline solutions examined continue throughout lengthened periods of time, especially when the liquid is from time to time replaced by fresh quantities of itself. After several weeks the action appears nearly to reach a maximum: from this point it proceeds with great slowness.

4. Exposure of a given surface of lead to increasing volumes of the same liquid does not materially influence the quantity of lead passing into solution, per unit volume of liquid.

5. The mechanical treatment to which the lead is subjected, very materially alters its powers of resisting the solvent action of dilute saline solutions. M. M. P. M.

Silicofluorides of Iron and of Cobalt. By F. STOLBA (*Chem. Centr.*, 1876, 16—17).—The former salt is obtained by acting at a gentle heat on finely divided metallic iron with silico-fluorhydric acid; the crystalline mass is dissolved in water containing a few drops of silico-fluorhydric acid, and the solution is evaporated on the water-bath. The salt ($\text{FeSiF}_6 \cdot 6\frac{1}{2}\text{H}_2\text{O}$) forms large bluish-grey hexagonal crystals: when reduced to powder it has a sp. gr. of 1.961 at 17.5°: 1 part of the crystalline salt dissolves in 0.78 parts of water at 17.5°: it is rather less soluble in hot than in cold water.

The crystals undergo oxidation in moist air.

Cobalt silicofluoride ($\text{CoSiF}_6 \cdot 6\frac{1}{2}\text{H}_2\text{O}$) may be formed by dissolving cobalt carbonate in silico-fluorhydric acid, or by acting on barium silicofluoride with a boiling solution of cobalt sulphate.

The crystals are large, hexagonal, and of a red colour: they

effloresce very slightly in dry air. In the state of powder the salt has a sp. gr. of 2.113 to 2.121 at 19°: 1 part of the crystals is soluble in 0.847 parts of water at 21.5°. The salt is more soluble in hot than in cold water.

M. M. P. M.

Sublimed Molybdic Acid (Oxide) as an Object for the Polarising Microscope. By Dr. STIERLIN (*J. pr. Chem.* [2], xiv, 464).—Molybdic acid (trioxide) obtained by sublimation from ammonium phospho-molybdate affords a beautiful object for the polarising microscope.

G. T. A.

Mineralogical Chemistry.

Mineral Pseudomorphs. By FRANZ ENGEL GEINITZ (*Jahrb. f. Min.*, 449—504).—Taking as a foundation the exhaustive work of Blum (*Die Pseudomorphosen des Mineralreichs, mit 3 Nachträgen*), the author pursued his investigations further by submitting the specimens to a rigid microscopical examination, having three objects in view, viz.: 1. To ascertain whether a confirmation of the usual grouping or arrangement of pseudomorphs and a characteristic grouping of them according to their composition and mode of formation could be derived from a study of their microscopical enclosures, applying this question more particularly to "displacement pseudomorphs." 2. New data to be obtained in order to prove the regular progress of the changes taking place in the mineral. 3. To ascertain how far microscopical examinations would confirm or enhance macroscopical examinations.

Blum subdivides the displacement pseudomorphs into two groups, viz., "envelopment pseudomorphs" and "replacement pseudomorphs," but he says very little about a large class which the author terms "Ausfüllungs pseudomorphosen," or those formed by the complete filling up of the original mineral by the replacing substance. Blum however mentions pseudomorphs which have been formed first by envelopment and then by a filling up of the resulting hollow space.

"Envelopment pseudomorphs" often pass through two stages, first a real envelopment of the mineral or crystal takes place, when a perimorph is the result (Kenngott. *Uebers. Result. min. Forsch.*, 1856, 204), and this term applies equally when the substance of the original mineral remains unaltered, or is carried away. Secondly, the hollow space is filled up or partially filled up by the replacing substance. The enveloping substance may be the same in composition as the filling up substance, or more rarely it may have a different composition. The author proposes to modify slightly Naumann's arrangement and to class all pseudomorphs into five groups, the first three comprising all "alteration pseudomorphs," the last two comprising all "displacement pseudomorphs," as follows:—

1. Paramorphs, or pseudomorphs formed without the loss or addition of a constituent.

2. Pseudomorphs formed by the loss of a constituent.
3. Pseudomorphs formed by the addition of a constituent.
4. Pseudomorphs formed by the partial exchange of constituents, a distinct chemical relationship existing between the constituents of the original substance, and those of the replacing mineral.
5. Mechanical or hypostatical pseudomorphs, formed by a partial or complete displacement of the original substance, there being no chemical relationship between the constituents of the original mineral and those of the pseudomorphous mineral.

He is of opinion that a classification founded upon the chemical relationship existing between the constituents of the original mineral and those of the pseudomorph is the most likely to lead to satisfactory results, and he proposes to suppress the designation "displacement pseudomorph" in the sense in which Blum uses it. Blum's work is referred to throughout this communication as *Pseudom.*, I, II, III, being the work already mentioned above with the three supplements.

Chalcedony on Fluorspar, from France.—An incrustation of bluish chalcedony on fresh crystals of fluorspar, the point of contact between the two minerals being sharply defined, the surface of the chalcedony having a rough appearance owing to drusy quartz, and the edges and angles of the cubes of fluorspar exhibiting a rounded contour. Thin sections examined under the microscope showed that the fluorspar was slightly attacked on the outside, and that here and there a very narrow zone of small fibres of chalcedony standing at right angles to the faces was observed, other fibres radiating again from these at different points. These fibres belonged to botryoidal formations of chalcedony, the growth of which is distinctly seen by the very marked concentric rings or striæ observed. In the interior of the chalcedony mass crooked bundles of small fibres often occur, from which new fibres radiate towards the sides, and finally disappear in the surrounding chalcedony. Behrens (*Mikros. Untersuch. ü. d. Opale*; Sitzgsber. d. k. Akad. d. Wiss., Wien, lxiv, 4) describes a similar formation in milk-opal. The interior portion of this incrustation exhibits either smooth and even faces corresponding with those of the original crystal, or is drusy through small crystals passing inwards, or botryoidal through chalcedony, or lastly porous through the presence of thin quartz lamellæ situated in the position of the cleavage directions of the original crystal. The last occurrence is owing probably to the penetration of silicic acid on the cleavage-planes, the silica hardening and remaining whilst the substance of the original fluorspar was carried away.

Chalcedony after Calcite from Schneeberg in Saxony. (Blum, *Pseud.*, 250.)—These pseudomorphs consist of smooth or slightly botryoidal groups of brown crystals built up of two obtuse rhombohedrons with a very short prism. Some of these crystals are filled up with chalcedony, and others are empty, the latter exhibiting a smooth interior face, which is really a "cast" of the original calcite crystal. The brown colour occurs only in the uppermost layer, the interior being colourless. The solid pseudomorphs show very clearly and beautifully the process of alteration, viz., first the envelopment and hollowing out of the original crystal, and lastly the filling up of the hollow

"cast." A microscopical examination revealed the fact that the outer shell was composed of several parts, viz.: 1. Small grains of quartz lying in clear, sharply defined lines nearest to the original calcite; 2. Next to the quartz grains are either rows of colourless quartz crystals or pyramidal faces or colourless fibres of chalcedony, which occupy a position at right angles to the crystal face of the original calcite crystal, terminating however parallel with this face at a greater distance in the interior of the mass; 3. Immediately after the colourless layer last described, there is a layer of brown globular fibrous chalcedony. The dark colour of the chalcedony is produced by the interposition of small brown laminæ of ferric oxide, which are often curiously grouped and serve occasionally as a nucleus for radiating sheaves of chalcedony fibres. Small colourless, double-refracting crystalline masses exhibiting the characteristic angle of calcite, are often observed in the interior of the chalcedony substance; they have not the appearance of having been attacked by solvents, but point unmistakably to a simultaneous formation with the chalcedony, so that the solution of the original calcite and the refilling of the hollow space thus formed took place probably about the same time. This pseudomorph is not composed of hornstone but of brown, globular, fibrous chalcedony, thus confirming Breithaupt's statement (*Paragenesis der Mineralien*, Freiberg, 1849, p. 223).

Hornstone after Calcite, Schneeberg. (Blum, *Pseud.*, p. 250.)—A macroscopical examination showed this pseudomorph to be built up as follows: 1. A layer of quartz crystals resting immediately upon the obtuse rhombohedral faces of the original crystal, and this again enveloped by bluish chalcedony; 2. Towards the interior, and next to the quartz crystals mentioned above, there is a sharply defined narrow zone of colourless quartz enveloping the original crystal, and the remainder of the crystal mass consists of reddish, splintery hornstone occurring mostly in globular aggregations. Under the microscope the hornstone was found to owe its red colour to the intermixture of brownish-red, translucent, ferric oxide, occurring either in light globular forms, or pulverulent, sometimes also in small crystalline concretions in the centre of individual globules. Hornstone may therefore be said to afford one of the best examples of colour produced by mechanical intermixture of foreign colouring matter. Small, colourless, crystalline fragments of calcite were also observed in the middle of the spherules of chalcedony, as in the last-mentioned pseudomorph.

Quartz after Fluorspar, Cornwall. (Blum, *i.*, p. 129.)—The specimens described by W. Fox and Blum differed from the specimen examined by the author in containing, here and there, a residue of the original fluorspar, either in etched pieces or perfect octohedrons. Fox described the parallel layers of quartz of different kinds observed on some of his specimens, and was of opinion that the siliceous matter was deposited in intervals of more or less duration, or at least under varying circumstances. The author considers the solution of this curious deposition is to be found in the well-known "zonal construction" of some of the crystals. An examination of his preparation showed that the outer crust was narrow, colourless, and white,

consisting of quartz rendered opalescent by fluid enclosures; parallel with this crust were three white, opaque bands, the central one being very sharply defined, whilst the other two were not nearly so distinct. Immediately underneath the outer crust, there is a mathematically straight line (corresponding with the smooth surface of the original crystal), and above and below this line there is a zone of small quartz grains, the commencement of the pseudomorphous formation being seen in the outer zone of quartz crystals, which increase in size from the straight line towards the outer surface of the pseudomorph. From the straight line towards the interior the three white, opaque bands are observed occurring at regular intervals, and separated by zones of quartz crystals. The central zone of quartz crystals was broken into or disturbed in one place, causing a confused arrangement of large and small crystals to take place, the inner hard lamella or band (separating the central quartz zone from the lower one) was also penetrated, thus allowing the solution of silicic acid to flow through. The quartz crystals in all the zones have a position perpendicular to the outer crust. The author concludes from his examination, that the "zonal construction" of certain fluorspar crystals offers great facilities for the formation of pseudomorphs by replacement, as "weathering" and decomposition take place mostly in these zones. A solution of silicic acid penetrates the outer surface of the crystal, incrusting it outside and inside with quartz crystals, the fluorspar substance disappeared eventually, leaving a hollow space closed at the bottom by a zonal lamella (parallel with the outer crystal face): then another entrance of silicic acid solution occurred, filling up the hollow space with quartz crystals. Silica, also, entered at all the other zonal lamellæ through minute cracks, incrusting the surface of the lamella first, and then gradually forming a zone of crystals, as in the first-mentioned case, a communication being set up between one zone and another by the fracture of the lamella.

Quartz after Fluorspar, from Rothenburg, near Schwartzenberg, Saxony. (Blum, *Pseud.*, p. 230.)—Occurs on quartzite, together with fibrous hematite, the sharply-defined cubes being thinly encrusted with ferric oxide, which is also found here and there in the interior of the crystal. The mass of the crystal consists of irregularly distributed quartz grains, which contain an extraordinary number of fluid enclosures and hollows distributed in straight parallel lines, the white colour of the grains being caused by their number. All these lines are situated in individual grains, and do not pass over to a neighbouring grain. There was no residue of the original fluor spar, and as the distribution of the quartz grains was irregular and not perpendicular to the outer crystal face, it is scarcely possible to explain the formation of this pseudomorph.

Semi-opal and Quartz after Calcite, from Leisnig, Saxony. (Blum, iii, p. 229.)—This specimen was an excellent example of the formation of a pseudomorph by "incrustation," and final filling up (*Ausfüllung*), as the scalenohedrons occurring upon it were filled up with fresh brown semi-opal, the exterior of this opal being weathered and of a yellowish-white colour, and immediately next to the weathered semi-opal, there was a cap of a brittle scaly mass of the same substance,

and this, again, was enclosed by fresh bluish quartz. The pseudomorph was formed by the original calcite crystal being first enveloped by the scaly semi-opal; the calcite was displaced and carried away, and the hollow space thus produced was then filled up with the brown semi-opal mass, the whole finally enclosed in quartz. The line of demarcation between the fresh and the weathered opal was sharply defined. The opal in the interior of the crystal was individually colourless, but it appears mostly of a liver-brown colour, through the presence of glimmering particles of hydrated ferric oxide, and sometimes it is whitish and opaque, owing to the presence of numerous cracks and hollows. Quartz occurs in some places in the brown opal, in rounded grains, angular masses, and crystals completely developed above and below. Occasionally, globular masses of colourless drusy hyalite were also observed. Larger masses of colourless quartz were present here and there in the brown opal, containing fluid enclosures and particles of hydrated ferric oxide, and projecting from the opal mass in the form of calcite rhombohedrons. These masses exhibited a beautiful play of colours in stripes, parallel with the edges when examined in polarised light, which proves that they consist of quartz entirely and not of calcite. Some of these forms projected also out of the colourless quartz substance.

Chalcedony after Fluorspar, from Trestyan, Siebenbürgen. (Blum, *Pseud.*, p. 244). (Behrens, *Opale*, p. 39). (Naumann, *Mineralogie*, p. 225). The crystals of this pseudomorph appear, sometimes, smooth and sharply defined, also dull, with edges and angles rounded off. Some are also found in globular forms having impressions on one side of sharply-defined cubes, which they formerly enveloped. Under the microscope, these cubes appeared to consist mostly of fibrous chalcedony; sections were taken perpendicular to the outer chalcedony mass, and examined with the following result. Below the outer crust, there were several curved layers of globular masses of chalcedony fibres, upon which rested small crystals of quartz. After these layers followed quartz-grains, increasing in size upwards, and terminating in lines intersecting at right angles, and upon these lines rested a zigzag zone of small cloudy grains of quartz. Upon this zone were arranged long fibrous crystals of quartz, their terminals producing a fine line of demarcation, upon which rested a broad zone of milky chalcedony, consisting mostly of fibrous granules and a narrow line of small clouded crystals, which terminated finally in a layer of pellucid chalcedony, constituting the outer surface of the crystal. It will thus be readily seen that the intersecting rectangular lines with their accompanying zones, coincide with the limits of several cubes of different sizes; the fibrous formations are all perpendicular to the lines. The author discovered, also, the presence of extremely small colourless crystals in the colourless and milky chalcedony layers in very large numbers, some being 0.03 mm. in diameter, and from a careful examination, he concluded that they were fluor-spar crystals, as their crystal form and behaviour in polarised light seemed satisfactorily to prove. They are, certainly, not a residuum of the original fluor-spar mass, but a formation simultaneous with the chalcedony. The above results serve, therefore, to show that the

statements of Mohs, Phillips, Ferber, and others, are erroneous, they having held the opinion that these pseudomorphs were really rhombohedrons of *quartz*.

Quartz after Calcite, locality unknown.—This pseudomorph was probably an example of exchange of a constituent, a chemical relationship existing between the two minerals. The crystal was a scalenohedron, 2 cm. in length, coated on its outer surface with small brown shining crystals, which proved to be rhombohedrons of calcite, slightly coated in their turn by a film of quartz, as their outer surface was not readily acted upon by acids. The interior of the crystal consists of quartz-grains, which are occasionally distributed in such a way as to form lines corresponding with the cleavage-directions of the primary rhombohedron of calcite. Enclosed in the quartz mass are small crystals of galena and zinc-blende, 0.4 mm. in size, also fluorspar crystals. A pseudomorph, described by Blum (*Pseud.*, p. 235, and i, p. 134), closely resembles the specimen described above.

Gypsum after Rock-salt. Gössling, Upper Austria. (Blum, *Pseud.*, p. 222, i, p. 125.)—This crystal was a flattened cube with concave faces, and contained crystal grains of calcite, quartz, and gypsum. The quartz was colourless and did not contain fluid enclosures. The interior consisted of gypsum individuals enclosing fluid in the parallel layers peculiar to that mineral. No chloride of sodium could be detected. The pseudomorph in question was probably formed by envelopment by clay and filling up by gypsum.

Chalcedony after Datolite, Haytor, Derbyshire. (Blum, *Pseud.*, p. 56, iii, p. 49.) A section of a yellowish crystal of so-called Haytorite, parallel to the face $2\bar{P}\infty$, was prepared and examined under the microscope. A very narrow zone of chalcedony fibres was found to run parallel with the outer crystal face, the fibres being at right angles to the latter. The interior consisted of irregularly distributed fibrous chalcedony and fluid enclosures (the latter being occasionally in parallel layers). Quartz grains were also observed, and the author concludes, from the finely fibrous structure of the chalcedony and the sharply-defined outer crystal form, that the pseudomorph arose by a gradual change and replacement without envelopment.

Green Earth (Glauconite) and Calcite after Augite, Fassathal, Tyrol. (Blum, *Pseud.*, p. 217, i, p. 210.)—In the porphyry of this district there are crystals of augite which have been converted into "green earth and calcite," the former producing a narrow layer on the outside and retaining the sharply defined form of the original crystal, whilst the latter constitutes the greater part of the crystal interior, which consists mostly of white cleavable individuals. The calcite never penetrates to the outer augite crystal, there being always a zone of green earth covering it, and often penetrating the calcite mass in cracks corresponding with the cleavage directions, and coating them with a green film, thus sharply defining the individual crystals of calcite. Magnetite crystals occur numerously in both the green earth and also in the calcite in regular stellar groups; they also occur in the decomposed porphyry, thus proving their recent formation from augite. The calcite and green earth occur in varying proportions, the former predominating in some cases and the latter in others, and they

not only occur together in these pseudomorphs, but also filling up hollows in the surrounding rock, as a section of the augitic porphyry from Marienberg showed hollows filled up with calcite in crystals, and covered by a layer of green earth. Blum says that the augite was displaced by calcite, but the author concludes from microscopical examination that the green earth and calcite were formed simultaneously, the crystal form of the original mineral being retained through the chemical action being limited to the interior of the crystal, owing to the outer coating of green earth.

Brown Iron Ore (Hydrated Ferric Oxide) after Iron Pyrites, Göttingen.—Some of the cubes of this specimen exhibited, on being broken, a still fresh interior, consisting of shining or tarnished pyrites surrounded by a small zone of brown iron ore. A section of one of these crystals showed that numerous minute brown veins of the latter substance penetrated the inner pyrites mass in every direction, proving that the decomposition progressed gradually from the interior.

Brown Iron Ore after Iron Pyrites, Schindelberg, near Osnabrück. (Blum, *Pseud.*, iii, p. 184.)—The cubical crystals of this specimen exhibit a coarse parallel striation, the faces being convex. A cleavage made parallel to a cubical face shows the crystal to have the following structure, viz., immediately next to the outer surface there is a narrow zone of earthy dull brown iron-earth, and a thin strip of shining iron pyrites passes from each angle of the section towards the centre. These strips do not pass through the angles, but terminate in some point in the brown iron zone. They have therefore the appearance of a reclining cross when the crystal is cleft through the middle, the arms of which intersect in the centre of the crystal, or else impinge upon a small sharply defined cube, which can be easily separated from the other portions of the crystal. If the cleavage has not been made through the centre of the crystal, the strips impinge upon the angles of a dark coloured square in the interior of the crystal, the sides of the square consisting of shining undecomposed iron pyrites. There appears a more decided zone of decomposition into brown iron ore in the angles of the triangles formed by the intersecting shining strips situated immediately next to the centre of the crystal. Occasionally this decomposition has made so much progress that only three zones are observed, viz.: (1) the outer surface; (2) a shimmering zone of iron pyrites; (3) a zone of decomposed iron pyrites (brown iron ore), the square face in the centre having disappeared. From this peculiar structure it may be inferred that the cubes of iron pyrites were most easily decomposed in directions passing from each face towards the centre, forming a negative four-sided pyramid. If the brown iron ore of one of these crystals be dissolved out by means of hydrochloric acid, funnel-shaped hollow crystal faces are obtained, corresponding with those observed in nature. The iron pyrites is penetrated by veins of brown iron ore, having a parallel position to the cubical edges or an octohedral face.

Malachite and Chessylite, after Cuprite, Chessy, near Lyon. (Blum, *Pseud.*, 39, iii, 34, *Pseud.*, 215.) (Reuss, *über einige Pseudomorphosen Sitzber. d. K. Ak. d. Wiss., Wien*, 1853, x, 63.) (Sillem., *N. Jahrb. f. Min.*, 1851, 386.) (Zirkel, *Mikr. besch.*, 101.)—An examination of

this pseudomorph proved that in most instances chessylite was formed first, and from this again the malachite, therefore they are two consecutive formations. Occasionally, however, both are simultaneously formed. The malachite was observed occurring in the regular forms described by Zirkel, and the chessylite in irregular crystalline lines of demarcation in the cuprite mass. Sometimes the chessylite is immediately adjacent to the cuprite, at others separated by a strip of malachite, so that a crystal of original cuprite occurs with its solid angles and outer surface consisting of chessylite, next to this a narrow zone of malachite, the interior consisting of unaltered cuprite. It must not be inferred from this that the chessylite is a later formation, since crystalline particles of malachite have also been observed penetrating chessylite.

Arragonite after Gypsum, Mansfeld, Thuringia. (Blum, *Pseud.*, 47, iii, 46.)—Occurs in accumulations of small thin crystals arranged with their vertical axes parallel. In contact with the gypsum the crystals of arragonite occur singly and penetrating; some are even embedded in it and isolated. Some of these crystals exhibit regular depressions, and over all of them are observed the straight cleavage lines of the gypsum. From the above it may be safely concluded that the arragonitic substance crystallised out at once, without hindrance in the gypsum mass.

Zonal Structure and the Formation of Pseudomorphs.—Some crystals of orthoclase from the porphyry of Borneo exhibit a distinct zonal structure, the outer surface or zone consisting of a white product of decomposition, the inner zone being clear. Small cracks and rifts were observed (on examination of sections under the microscope, passing from the exterior to the different innermost zones, a deposit of kaolin occurring along these zone surfaces, so that it is quite apparent that the decomposing force came from the exterior. A similar decomposition is observed occurring in triclinic feldspars, the twin striation lending itself readily to the decomposing action of water, &c.

Calcite after Gaylussite, Sangerhausen, Thür. (Blum, *Pseud.*, 13.) (Naumann, *Min.*, 9, Aufl., 247.)—A section examined under the microscope showed the structure of this pseudomorph to be as follows. A series of parallel zones of calcite, retaining the outer contour of the crystal, the substance of these zones being principally colourless rhombohedrons here and there with a grain of quartz between them, and irregularly distributed sheaves and groups of fine needles and prisms of a greenish-white colour, which may be a residuum of the original mineral.

Tinstone after Orthoclase, St. Agnes, Cornwall.—The outer zone consists of perfectly clear quartz, and below it there are irregularly distributed crystals of tinstone. Several zones were observed retaining the outer contour of the crystal. Sometimes the quartz predominates over the tinstone, whilst at other times the contrary is the case, a fact which argues strongly that it is a case of pseudomorphism by displacement.

Parasite (?) after Boracite.—After quoting the work of Volger (*Pegg. Ann.*, 92, 1854, 77) and others upon boracite, the author gives the results of his investigations of crystals from Lüneberg, exhibiting

the form $\infty 0 \infty . \infty 0 . \frac{0}{2}$, briefly as follows. A sharply defined inner

kernel was observed surrounded by an outer shell, which here and there vanished, causing the kernel to be still more sharply defined. This outer shell consists of clear or clouded grains of boracite, together with a fibrous formation at right angles to the outer crystal faces. The shell is whitish or opaque on the rhombic dodecahedron faces, whilst the cubical faces are transparent. In undecomposed crystals the inner kernel appears to be colourless and filled with fragmentary angular deposits of the same boracite substance as the surrounding shell. Sections of decomposed crystals made parallel to a cubical face exhibit the internal kernel divided into four fields by straight bundles of fibres situated at right angles to the rhombic dodecahedral faces, and cutting each in the centre. These fibres terminate at a slight distance from the outer surface of the kernel. Independently of these fibres, the author observed in undecomposed as in decomposed boracite crystals from Lüneberg and Segeberg, colourless, lenticular, spear-like groups of needles intersecting each other nearly at right angles, which were doubly refractive. The colourless substance surrounding the above-mentioned fibres and needles appears mostly of a light bluish-grey colour, and an examination of the perfectly colourless crystals from Stasfurt showed the same fibre formation, G. Rose being of opinion that they were pseudomorphs of stasfurtite enclosed in boracite. The author concludes from his results that the fibres are a secondary formation, the outer surfaces of the undecomposed boracite crystals being clear, therefore they cannot be pseudomorphous.

Sanidine after Leucite. Ober-Wiesenthal, im Erzgebirge. (Naumann, *N. Jahrb. f. Min.*, 1860, 61.) (Blum, iii, 71, *Pseud.*, 64 and ii, 23.) Zirkel, *Pogg. Ann.*, 1869, Bd. 136, 545.)—This pseudomorph was tinted in places by ferric oxide, and contained numerous pellucid particles arranged in strips and separated by more opaque substance. Examined under the microscope these particles proved to be crystalline grains, never exhibiting any crystal form, but often oblique cracks. In polarised light they generally appear to be colourless, blue, or brown-red. From other characteristic appearances, the author concludes that these particles were sanidine, and not leucite. In the colourless portions of the pseudomorph were stellar aggregations of a whitish clouded product of decomposition, and on the edges of drusy spaces in the colourless mass were stellar aggregations of potash mica. Nosean was also met with in some specimens.

Rock Salt after Carnallite or Sylvite (of v. Zepharovich). (Weiss, *Zeitsch. d. d. Geol.*, Gest. 25, 558; v. Zepharovich, *Min. Mitt. v. Sitzb. d. k. Akad., Wien*, 1874, Bd. 69, 7—11.)—The author confirmed the statement made by Weiss in the most conclusive manner, having found that the red colour of this pseudomorph is owing to the presence of a large quantity of hexagonal plates and streaks of blood-red ferric oxide.

Muscovite after Prosopite and Topaze, Schlaggenwald. (Blum, iii, 58, *Pseud.*, 66, ii, 137; *Pseud.*, 254, iii, 231.) (Scherer, *Pogg. Ann.*, 1853, 90, 315.) (Hausmann, *Pogg. Ann.*, 1854, 92, 612.)—The original mineral (which was attached to fluorspar) when examined under the

microscope was observed to be decomposed into two different substances which had originated out of each. The prosopite substance was penetrated by numerous cracks and rifts, which were clothed by small short sheaves and radiating groups of dirty yellow needles or plates, these sheaves and bundles often enveloping small portions of unaltered prosopite; and out of this product of decomposition projected sheaves of bent, colourless, or greenish fibres, which proved to be nacrite (muscovite). Where these nacrite masses impinge upon the first-mentioned product of decomposition, portions of the latter penetrate the former, thus showing that nacrite is the primary product.

Lithomarge (?) after Fluorspar.—Locality unknown. Some of the faces of the fluorspar cubes are white and opaque, and covered with an earthy deposit, which consists of colourless prismatic crystals. These crystals penetrate inwards, and are also arranged in a layer in undulating lines near the outer surface of the crystal, in connection with a violet-coloured zone. With these crystals bundles of nacrite crystals occur simultaneously, also a mass of dirty-yellow needles. It will be seen that a decomposition has taken place in this case similar to that which was observed in nacrite after prosopite. The white opaque outer mass showed all the characteristics of lithomarge. Another specimen exhibited the occurrence of these crystals in sharply defined zones, from which the author concludes that they were enclosed by the growing fluorspar crystal, as they are mostly isolated in the unaltered substance.

Nacrite (Muscovite) and Fluorspar after Prosopite, Altenberg, Erzgebirge. (Blum, iii, 54.) (Scheerer, *Pogg. Ann.*, 90, 315.)—A section of a crystal made parallel with the face, $\infty P \infty$, exhibited a straight line commencing at the terminal angle of the pyramid, and running parallel with the vertical axis. The upper portion of the decomposed crystal was divided into sharply defined parallel strips, which projected unhindered past the straight line (zwillingsnaht) mentioned above. The interior of the crystal is colourless or brownish, and contains numerous sheaf-like groups of nacrite crystals, which are situated at right angles to the parallel strips and between them. Fluorspar crystals occurring in the mass of the crystal were also observed.

Paramorphs.—The author states that no satisfactory results have been obtained from the microscopical examination of numerous specimens, and recommends further research into this branch of pseudomorphism.

From the results obtained the author considers—(1) that mineral pseudomorphs must be classified according to the chemical relationship existing between the original mineral and pseudomorph; (2) the name "displacement pseudomorph" is not sufficiently comprehensive; (3) the apparent internal decomposition often observed stretching towards the outer surface is caused by cracks and rifts penetrating the interior of the crystal.

The author appends numerous drawings illustrating his paper.

C. A. B.

The relation of Franklinite to the Spinel Group. By G. H. SEYMS (*Amer. Jour. of Sci.* [3], xii, 210).—The object of the following investigations was to determine whether the variation of the amount of iron which occurs in Franklinite, as shown by many analyses, affects the general character of the mineral, and also to supplement recent investigations upon its composition and relation to the spinel group. The first experiments were made on perfectly formed crystals in a matrix of lime-stone, the mean of the analyses giving—

	Fe ₂ O ₃ .	Mn ₂ O ₃ .	MnO.	ZnO.
0.17	63.40	4.44	10.46	23.11 = 101.58

The relation of the metals to the oxygen calculated from this analysis would be—

	Metals.	Oxygen.
Fe ₂	44.38	19.02
Mm ₂	3.09	1.35
Mn	8.10	2.36
Zn	18.55	4.56
		20.37

Dividing by the atomic weights, the ratio of metals to oxygen would be R : O :: 3 : 3.999, nearly equal to R₂O₃, or an oxygen-ratio of the protoxides to sesquioxides of 1 : 0.981, or nearly 1 : 1, corresponding to the formula of the spinel group (R₂O₃ + RO = R₃O₄). The state of oxidation of the manganese was determined by the solution of the mineral in hydrochloric acid, and the estimation of the chlorine liberated by Bunsen's iodine method, the mean of these results being 0.45, which requires the presence of 4.44 per cent. of Mn₂O₃.

A second sample gave as a mean of four analyses—

Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	ZnO.	MnO.
0.65	67.42	15.65	6.78	9.53 = 100.11

This giving as the relation between the metals and the oxygen:—

	Metals.	Oxygen.
Al ₂	0.35	0.30
Fe ₂	47.19	20.23
Fe	12.17	3.48
Zn	5.44	1.34
Mn	7.38	2.15
		20.53
		6.97

leading to the atomic ratio R : O :: 1 : 1.331, or 3 : 3.994 = R₂O₃, and showing the oxygen-ratio of protoxides to sesquioxides to be 1 : 0.981, or nearly 1 : 1.

As it has been stated that some varieties of Franklinite give with HCl a solution containing FeCl₂, at the same time evolving chlorine, the author tested the second sample by Bunsen's method with a negative result. The results of the analysis give in both cases a ratio very nearly corresponding with that of the spinel, notwithstanding the great differences in the relative amounts of iron, zinc, and manganese.

J. M. T.

A new Locality of Heavy Spar. (*Chem. Centr.*, 1876, 509).—In the Island of Mykone, near Syra, large deposits of very pure heavy spar occur, associated with manganese ores. M. M. P. M.

Strueverite. By A. BREZINA (*Chem. Centr.*, 1876, 501).—This mineral is essentially a silicate of iron and aluminium, containing also lime and magnesia, and traces of alkalis. It is found associated with gastaldite and baretite at S. Marcel in Piedmont. Structure, foliated and bent; colour, blackish-green; streak, greenish-white; hardness, between 6·5 and 7; scratches felspar, is scratched by quartz; specific gravity, 3·4; crystalline form, triclinic. This mineral is closely related to *sismondin* and *chloritoid*. M. M. P. M.

Gases contained in Meteorites. By A. W. WRIGHT (*Amer. Jour. of Sci.* [3], xii, 165—176).—The meteorites formerly examined by the author were of the stony and common type, containing a considerable percentage of nickeliferous iron, but no appreciable quantity of uncombined carbon. The meteorites of Alais, Kold Bokkeveld, Kaba, and Orgueil form a distinct class, containing a considerable quantity of amorphous carbon, and a bituminous substance consisting of carbon, oxygen, and hydrogen in such a way as to simulate organic products. The author has conducted these investigations to determine whether the conclusions drawn from his previous investigations are applicable to the bodies of this peculiar class.

The material used was a fragment of the Kold Bokkeveld meteorite. The method of obtaining and collecting the gases was the same as described in a former paper. As the meteorite gives off a large quantity of water on being heated, the tube containing the substance was connected with the pump by a recurved tube placed in a freezing mixture, so that the water was condensed, and could be reserved for examination. The temperatures were such as to avoid complication in the results. From decomposition of the bituminous matter the following are the results obtained:—

Kold Bokkeveld.

	CO ₂ .	CO.	CH ₄ .	H.	N.	Volumes.
300—350 ...	87·34	5·08	5·93	trace ?		7·45
500	95·53	1·32	2·14	0·54 ?	0·47	17·78

The amount of water driven off by heat and collected in the cooled tube, was found to be about 10 per cent. of the weight of the substance employed; this determination, however, was not entirely satisfactory. The water, on being tested, showed distinct presence of carbonic, and less distinct presence of sulphur dioxide.

The author gives a table of the gases found in different meteorites, both of the iron and stony class.

	CO ₂ .	CO.	CH ₄ .	H.	N.	Vol.	Observers.
<i>Iron meteorites.</i>							
Lenarto	4·46	0·00	—	85·68	9·86	2·85	Graham.
Augusta Co., Va.	9·75	38·33	—	85·83	16·09	3·17	Mallet.
Tazewell Co., Tenn.	14·40	41·23	—	42·66	1·71	3·17	Wright.
Shingle Spring, Cal.	13·64	12·47	—	68·81	5·08	0·97	"
Texas	8·59	14·62	—	76·79	0·00?	1·29	"
Dickson Co., Tenn.	13·30	15·30	—	71·40	0·00?	2·20	"
Arva	12·56	67·71	—	18·19	1·54	47·13	"
<i>Stony meteorites.</i>							
Iowa Co.	49·51	2·64	0·0?	48·93	3·92	2·50	"
Guernsey Co., Ohio.	59·88	4·40	2·05	31·89	1·78	2·99	"
Pultusk	60·29	4·35	3·61	29·50	2·25	1·75	"
Parnallee	81·02	1·74	2·08	13·59	1·57	2·63	"
Weston	80·78	2·20	1·63	13·06	2·33	3·49	"
Kold Bokkeveld.	93·11	2·42	3·25	0·38?	0·84	25·23	"

In this paper the author brings forward results with regard to the presence of CO₂ in the meteorites, which have modified to a certain extent his suppositions brought forward in a former paper. He considers it improbable that the CO₂ has been absorbed subsequently to the fall of the body, as in that case the carbonates formed would be stable compounds, and undecomposed by the low temperatures employed; the Iowa meteorite also shows a loss rather than a gain of CO₂ by lapse of time. An explanation was suggested in a former paper that the gas might be condensed upon the finer portions of the iron as well as absorbed in it; experiments have, therefore, been made to test the correctness of the supposition. The substance of the Iowa meteorite was reduced to powder, and the iron particles extracted with a magnet, thus dividing the matter into two portions; a third portion was also taken, consisting of the meteorite broken into small fragments. The following are the results obtained:—

	CO ₂ and CO.	H.	N.	Volumes.
Powder	66·96	30·96	2·08	0·97
Iron	38·72	59·38	1·90	0·51
Fragments ..	48·07	50·93	1·00	—
				1·48
				1·87

These numbers indicate that the powder contains a greater quantity of the carbon oxides than the iron, which, on the other hand, is richer in hydrogen. The product of the fragments are approximately the mean of the two others, but it will be seen that the volume obtained is somewhat larger, indicating that a certain loss of gas has taken place in the pulverisation. The author thinks that these facts indicate that while a portion of the gas may be condensed upon the finer particles of the iron, at the same time a large portion of the CO₂, probably also of the H₂O, CO, and other gases are imprisoned within it. The author also discusses the connection between meteorites and comets, as shown

by the close resemblance of the spectrum of the gas obtained from the stony meteorites to the spectra of those comets thus far observed.

J. M. T.

Formation of Natural Sulphuretted Waters. By E. PLANCHARD (*Compt. rend.*, lxxxix, 235—237).—Some confervæ taken from a sulphuretted mineral water were carefully washed and placed in a flask full of ordinary water. A week later, the water in the flask smelling distinctly of hydrogen sulphide, the idea suggested itself that the confervæ were the cause, and not the result, of the sulphuration of the water as had been before supposed, and experiments were instituted in order, if possible, to prove this hypothesis. In four flasks, pieces of lignite and various vegetable detritus were placed. In twelve others, a small quantity of the well-washed confervæ in equal proportions; all the flasks were then filled from the same solution of calcium sulphate, and corked.

The corks of four flasks containing confervæ were perforated with a glass tube drawn out to a fine point, which was sealed in the blow-pipe after the contents of the flask had been boiled for three minutes. In a week, the water in the eight flasks containing confervæ which had not been boiled, was strongly sulphurous. The water was thrown away, the confervæ well-washed, and the flasks refilled with solution of calcium sulphate. In eight days the sulphurous odour reappeared. The washing was repeated, and the operation continued in like manner for several weeks, during which time the confervæ continued regularly to effect the reduction of the sulphate, though in continually diminishing quantity.

In the flasks containing organic matter only, as well as in those which had been boiled, no sulphuretted constituents could be detected after the lapse of a month, but on introducing a small quantity of confervoid germs from one of the active flasks, rapid sulphuration of the water ensued. When a solution of calcium sulphate was used which had been previously well boiled, the sulphuration of the water was more quickly induced, hence the author thinks that the ferment lives at the expense of the combined oxygen when it cannot obtain oxygen in the free state, and that to this cause the reduction of the sulphate to sulphide is due. He does not, however, insist that the presence of sulphides or free hydrogen sulphide in mineral waters is, in every instance, the result of a similar reducing influence.

J. W.

Organic Chemistry.

Hydrocarbons of the Paraffin Series found in a Lava from Etna. By O. SILVERSTEI (*Gazzetta chimica italiana*, vii, 1—21).—In the basaltic zone to the S.S.E. of Etna, at a distance of 22 kilometers from the central crater, there is a very ancient lava stream, a dolerite of dark brown colour, almost basaltic in appearance, but which, when examined microscopically in thin section is seen to con-

sist of a crystalline base of augite, in which crystals of labradorite and peridote (olivine) are disseminated. In this lava there are cavities which, when broken open, appear filled with a liquid having the odour of mineral naphtha. Most of these cavities are small, but through Professor G. Pulvirenti, the author was enabled to secure the contents of a comparatively large cavity 10 cubic centimeters capacity, and also a supply of the lava from which this oily matter could be extracted by means of ether. The oil from the cavity had much the appearance of petroleum, being yellow by transmitted and green by reflected light. It was quite fluid at 24°, but at 17° it became almost solid from the deposition of crystals. The oil extracted by means of ether from the pulverised lava, which contained about 1 per cent. of it, was very similar, but contained a larger proportion of sulphur than that from the cavity. The solid crystalline matter separated from the oil by cooling it, was found to have the composition C_nH_{2n+2} ; it melted at 57° and boiled above 300°; its behaviour with solvents, and with various reagents was precisely similar to that of the so-called paraffin, whether prepared artificially or obtained from a natural source. The oil expressed from the crystalline mass was submitted to fractional distillation, when the higher fractions by cooling, &c., gave a further portion of solid paraffin melting at 52°, making a total of 42.79 per cent. of paraffin in the original oil. Of the liquid hydrocarbons, a very small portion, 0.74 per cent. boiled at 79–88°, the rest at 200–400°: besides these, the oil contained 4.39 per cent. of sulphur, and left 2.9 per cent. of pitch on distillation. The author then discusses various hypotheses, as to the formation of this petroleum, which seems to have a special volcanic origin, contemporaneous with the eruption which produced the lava. C. E. G.

Preparation of Chemically pure Grape Sugar. By C. NEUBAUER (*Chem. Centr.*, 1876, 516).—Finely powdered refined cane sugar is added to 500 or 600 c.c. of alcohol of 80 per cent., containing 30 or 40 c.c. of fuming hydrochloric acid, and the liquid poured off from excess of sugar, is set aside in a closed vessel.

Crystals of grape sugar are soon deposited; these are collected on a filter, washed with alcohol until free from acid, and dried by exposure on porous paper. The dry substance is recrystallised from boiling absolute alcohol. By adding a further quantity of powdered cane sugar to the acid mother-liquors, a second crop of grape sugar crystals is obtained. M. M. P. M.

Occurrence of Grape Sugar in Alcohol. By G. SALOMON (*Chem. Centr.*, 1876, 527).—Grape sugar has been detected by the author in the syrup obtained by boiling down alcohols of all kinds, even in absolute alcohol. He suggests that the sugar may be derived from the casks in which the alcohol is stored, these casks being often previously used for storage of liqueurs. M. M. P. M.

Silicon Sulphocyanate. By P. MIGUEL (*Chem. Centr.*, 1876, 516).—This substance is obtained in accordance with the reaction—



The action takes place on gently warming. The product is distilled: the distillate solidifies to crystalline needles, which are readily decomposed by moisture, melt at 241° , and boil at 300° . The compound is insoluble in ether, benzene, and carbon disulphide: it is dissolved and decomposed by potash.

M. M. P. M.

Action of Aromatic Substances on Excess of Iodine Chloride.

By V. MERZ and G. RUOFF (*Chem. Centr.*, 1876, 612).—Most of the members of the aromatic group, heated if possible to 360° with excess of iodine chloride, yield perchlorobenzene, and finally perchloromethane, or perchlorethane, or even both together. Phenol, cresol, thymol, &c., and even chloranil, easily yield perchlorobenzene, oxygen being given off as carbonic anhydride. Resorcin, camphor, and oil of turpentine give perchlorobenzene, whereas pyrogallic acid yields perchlorethane. Camphor and oil of turpentine can be formed from azobenzene, and from the three phenylenediamines, also from triphenylamine and its perchloro-derivatives. Perchlorobenzene can be produced from diphenylmethane, diphenylethane, anthracene, phenanthrene and naphthalene. Antimony pentachloride acts more energetically than iodine chloride.

E. W. P.

Chlorinated Derivatives of Benzene. By F. BEILSTEIN and A. KURBATOW (*Deut. Chem. Ges. Ber.*, x, 270—274).—When two, three, or four atoms of hydrogen in benzene are replaced by other substances, three isomeric products are possible, which may be distinguished as *symmetrical*, *unsymmetrical*, or *consecutive*, according to the position of the substituted atoms. The present paper describes the tri- and tetra-chlorinated derivatives of benzene, some of which have now been obtained for the first time by the authors.

TRICHLOROBENZENES.—1. *Unsymmetrical* (ordinary, 1 : 3 : 4).—First obtained by Jungfleisch by the action of chlorine on benzene. Obtained by the authors by treating dichlorophenol (melting at $42-43^{\circ}$) with phosphorus pentachloride, or by replacing by chlorine the amido-group in p-m-dichloraniline (melting at 71.5°), or in ordinary p-o-dichloraniline (melting at 63°). It melts at 16° and boils at 213° . When dissolved in strong nitric acid it yields *nitrotrichlorobenzene* melting at 58° . It dissolves in fuming sulphuric acid on warming, forming a *sulphonic acid*, of which the following salts have been prepared:—

$(C_6H_2Cl_3SO_3)_2Ba.2H_2O$. Long brilliant needles, very sparingly soluble in water.

$(C_6H_2Cl_3SO_3)_2Pb.2H_2O$. Crystallises from alcohol in small brilliant needles.

$(C_6H_2Cl_3SO_3)_2Ca.2H_2O$. Tufts of shining needles, very easily soluble in water.

2. *Symmetrical* (1 : 3 : 5).—Obtained by Körner by treating ordinary trichloraniline (melting at 77.5°) with ethyl nitrite, and by the authors in the same manner. It melts at 63.5° and boils at 208.5° ; dissolves sparingly in alcohol and acetic acid, freely in ether, carbon disulphide, and benzene; and yields with nitric acid a nitrotrichlorobenzene melting at 68° .

3. *Consecutive* (1 : 2 : 3).—Chlorine acting on metachloracetanilide produces the acetyl-derivatives of two isomeric trichloranilines, which admit of easy separation, owing to their different degrees of solubility in 50 per cent. acetic acid. The less soluble product is the acetyl-compound of unsymmetrical trichloraniline, the more soluble being the acetyl-compound of consecutive trichloraniline. These acetyl-compounds, when boiled with soda-ley, yield the free trichloranilines, the latter yielding p-m-o-trichloraniline (melting at 67·5°), which by treatment with ethyl nitrite is converted into consecutive trichlorobenzene. The last product melts at 53—54°, boils at 218—219°, and crystallises from alcohol in large tables. Its *nitro-derivative*, $C_6H_2Cl_3(NO_2)$ (1 : 2 : 3 : 4) forms silky needles melting at 55—56°, and yielding by reduction trichloraniline with consecutive chlorine-atoms.

TETRACHLOROBENZENES.—1. *Symmetrical* (ordinary, 1 : 2 : 4 : 5).—The authors obtain this substance from unsymmetrical trichlorobenzene by transforming it first into nitrotrichlorobenzene, and then into trichloraniline, and replacing the amido-group in the latter body by chlorine. It melts at 137—138° and boils at 243—246°. When dissolved in nitric acid it yields *nitrotetrachlorobenzene*, melting at 98°: at the same time some *chloranil* is always produced, which fact is characteristic of this body, chloranil not being formed by the action of nitric acid on the other tetrachlorobenzenes.

2. *Unsymmetrical* (1 : 3 : 4 : 5).—Obtained from ordinary trichloraniline by replacing NH_2 by Cl. It crystallises from alcohol in needles. Melts at 50—51°. Boils at 246°. With nitric acid of sp. gr. 1·52 it yields a nitro-derivative melting at 21—22°.

3. *Consecutive* (1 : 2 : 3 : 4).—Obtained by replacing by chlorine the amido-group in trichloraniline with consecutive chlorine-atoms. Needles, melting at 45—46°. Boils at 254°. It yields a nitro-product which is reduced by tin and hydrochloric acid to tetrachloraniline melting at 118°. J. R.

Propylbenzene and Propylphenol. By E. PATERNO and P. SPICA (*Gazzetta chimica italiana*, vii, 21—24).—The propylbenzene was obtained by gradually adding pure benzyl chloride, prepared from pure benzyl alcohol, to zinc-ethyl slightly warmed, in equivalent quantities: the excess of zinc-ethyl was then decomposed by water, hydrochloric acid added to dissolve the zinc oxide, and the hydrocarbon distilled off in a current of steam. Although it was digested for several days with sodium and subjected to repeated fractional distillation, the authors were unable to obtain a product of constant boiling point, owing in all probability to the presence of a minute quantity of unaltered benzyl chloride, which could not be removed. The normal propylbenzene prepared in this way boiled at 156·5—158·5° (cor.) under a pressure of 758 millimeters. Its density at 0° was found to be 0·881, almost identical with that of cumene from cumenic acid, namely 0·879. The *sulphonic acids* were formed on dissolving the hydrocarbon at a gentle heat in a mixture of ordinary and fuming sulphuric acid. The two isomeric *barium salts* corresponding to the two acids were separated by fractional crystallisation; the α -salt crystallising in anhydrous laminae, the β -salt which is the more soluble, in tufts of microscopic prisms

containing $2\text{H}_2\text{O}$. The *lead salts* were prepared from the barium salts by decomposing them with sulphuric acid, and subsequently neutralising with lead carbonate; the α -salt contains H_2O , and crystallises in plates resembling the α -barium salt: the β -salt, which is much more soluble, in laminae containing $2\text{H}_2\text{O}$.

Propylphenol.—This compound was prepared by fusing the potassium salt of α -propylbenzene-sulphonic acid with potassium hydrate in the usual manner. It is an oily compound boiling at about 230° . Its methyl derivative boils at 210 — 215° . C. E. G.

Cresols and Cresotic Acids. By R. IHLE (*J. pr. Chem.* [2], xiv, 442—464).—The author prepares cresol from commercial phenol of high boiling point or cresylic acid. The naphthalin is removed by treating the crude substance with dilute caustic soda, filtering and passing steam into the filtrate. The phenol is got rid of by adding baryta-water, since cresol is possessed of weaker acid properties than phenol.

Cresols can also be prepared from the toluidines by the following process. The nitrate is mixed with water till a thick liquid is formed, which is then divided into separate portions, through which nitrous acid is passed till they become liquid, and the acid is no longer absorbed, the temperature being all the time kept below 30° . Sulphuric acid diluted with twice its bulk of water is then added to the solution, together with three times the volume of absolute alcohol. On addition of a sufficient amount of ether, the sulphates of the diazo-compounds separate in fine crystals.

These are next dissolved in water and heated for some time on the water-bath. The oily layer which rises to the top is removed, and the liquid shaken up with ether. The cresol is then submitted to fractional distillation. The cresotic acids are obtained by treating the sodium compounds of the cresols with carbon dioxide in the same way as Kolbe prepares salicylic acid.

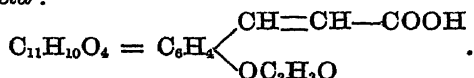
Coal-tar cresol yields two cresotic acids, one of which melts at 173° , the other between 115 — 120° : hence there are two isomeric cresols in coal-tar. The cresol corresponding with solid toluidine, with a melting point of 36° and boiling point of 198° , yields a third cresotic acid which melts at 148° . A fourth cresotic acid can be obtained from the cresol corresponding with liquid toluidine, which melts at 30° and boils at 188° . This acid has a melting point of 159 — 160° .

The behaviour of potassium towards the cresotic acids is not the same as towards salicylic acid. For whereas the latter is converted by heating its potassium salt to 220° into paraoxybenzoic acid, the cresotic acids—except the one which melts at 159° —do not undergo a similar molecular alteration, one cresotic acid being converted into another which is isomeric with it. G. T. A.

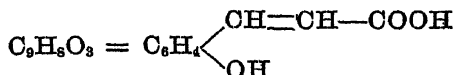
Synthesis of Coumarin from Salicylic Aldehyde. By FRED. TIEMANN and H. HERZFELD (*Deut. Chem. Ges. Ber.*, x, 283—288).—The authors have previously shown that paraoxybenzaldehyde, when heated with acetic anhydride and sodium acetate, yields acetylparacoumaric acid; and that benzaldehyde, when similarly treated, yields

cinnamic acid. The same reaction has now been extended to orthoxy-benzaldehyde (salicylic aldehyde).

When a mixture of salicylic aldehyde (3 parts), acetic anhydride (5 parts), and sodium acetate (4 parts) is gently heated for some hours, the whole solidifies on cooling to a crystalline mass, from which, on treating it with water, there separates an oil smelling of acetic acid and coumarin. An ethereal solution of this oil, when shaken with a solution of sodium carbonate, gives up thereto a crystallisable acid, whilst coumarin remains dissolved in the ether. The acid dissolves easily in hot water, alcohol, and ether, and crystallises from water in white needles, which melt at 146° and have the composition of *acetyl-orthocoumaric acid* :

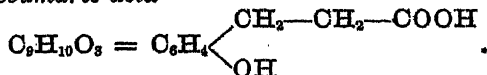


Acetylorthocoumaric acid is resolved, by heating with weak potash-ley, into acetic acid and *orthocoumaric acid*—



The latter crystallises in white needles melting with decomposition at $207-208^{\circ}$.

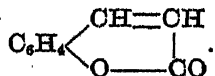
Orthocoumaric acid is converted by treatment with sodium-amalgam into *hydro-orthocoumaric acid*—



which crystallises in large pointed needles melting at $82-83^{\circ}$.

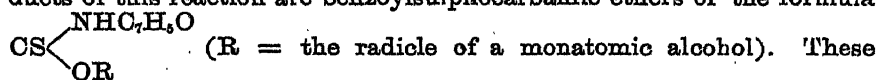
Acetylorthocoumaric acid, when gently heated above its melting point, evolves pungent fumes of acetic acid, and ultimately leaves a thick oily body, an ethereal solution of which deposits crystals of coumarin on evaporation.

In accordance with these results the constitutional formula of coumarin is—

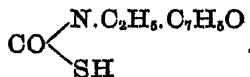


J. R.

Action of Alcohols of the Fatty Series upon Benzoylsulphocarbimide. By P. MIGUEL (*Chem. Centr.*, 1876, 516).—The products of this reaction are benzoylsulphocarbamic ethers of the formula

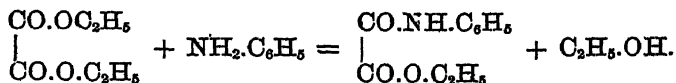


ethers form salts with alkalis. The ethyl-compound is identical with the substance which Lössner obtained by the action of benzoyl chloride upon an alcoholic solution of potassium sulphocyanate. The author doubts the correctness of Lössner's formula, viz. :



M. M. P. M.

Action of Phosphorus Pentachloride on Phenyl and Paratolyl-oxamethane. By H. KLINGER (*Liebig's Annalen*, clxxxiv, 261—289).—Ethyl oxalate and aniline were mixed and heated to gentle ebullition in a reflux condensing arrangement in the proportions required for the reaction—



The temperature did not rise much above 120°, on account of the alcohol thus produced, and the reaction was completed in four to five hours, 250 grams of ethyl oxalate and 156 of aniline being employed. On cooling the mass solidifies completely to a yellowish-white crystalline substance, which becomes white after washing with 90 per cent.

alcohol. The *oxanilide*, $\begin{array}{c} \text{CO.NH.C}_6\text{H}_5 \\ | \\ \text{CO.NH.C}_6\text{H}_5 \end{array}$, thus produced melts at 245°;

the washings deposit a little more oxanilide on standing, and on evaporation, the filtrate from this forms crystals of *ethyl phenyloxamate*

(phenyloxamethane), $\begin{array}{c} \text{CO.NH.C}_6\text{H}_5 \\ | \\ \text{CO.O.C}_2\text{H}_5 \end{array}$. The yield of this body is from

70 to 80 per cent. of the calculated amount; it melts at 66—67°, and is readily soluble in hot carbonaceous solvents, also to some extent in water, from which it crystallises in long slender white needles, melting at 65°; for the most part it distils unaltered at 260—300°. When dissolved in alcohol, this ether is readily acted on by aniline and by ammonia, which produce precipitates consisting of *oxanilide* and *monophenyl oxamide* respectively; alcoholic potash readily saponifies it, forming potassium phenyl oxamate, from which *phenyloxamic acid*

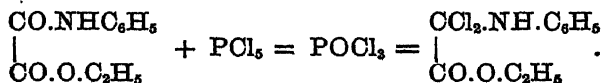
(oxanilic acid), $\begin{array}{c} \text{CO.NH.C}_6\text{H}_5 \\ | \\ \text{CO.OH} \end{array}$, is readily prepared by decomposition

with hydrochloric acid and purification by crystallisation from hot water, or better, from benzene, the body being less soluble in the latter menstruum; it melts at 149—150°, and when crystallised from ether at 150—151°; the crystals obtained from water contain one molecule of water of crystallisation. The barium and calcium salts are readily obtained by precipitating the aqueous solution of the acid by barium or calcium chloride; the former forms small plates, shining like mother-of-pearl, the latter shining white needles, often stellate.

On treatment with bromine, *ethyl bromophenyloxamate*, $\begin{array}{c} \text{CO.NH.C}_6\text{H}_4\text{Br} \\ | \\ \text{CO.O.C}_2\text{H}_5 \end{array}$,

is formed; this is best obtained by dissolving ethylphenyloxamate in carbon disulphide, and cautiously adding the calculated quantity of bromine; an oily substance then separates, which shortly becomes a crystalline mass; after crystallisation from alcohol, the substance melts at 154—156°; on saponification it forms Mills's *bromaniline*, melting at 61—62°, and identical with that produced by saponifying brominated phenylacetamide.

When acetyl chloride is made to react on ethyl phenyloxamate, $\text{CO.N(C}_2\text{H}_5\text{O).C}_6\text{H}_5$, is formed, melting at 64—65°; pentachloride of phosphorus gives rise to the formation of *phenylamido-dichloroacetic ether*, in virtue of the reaction—

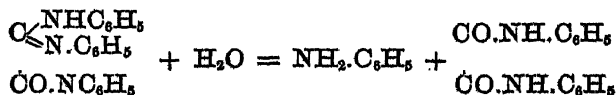


No gas is evolved during this change; to obtain the best result the ethyl phenyloxamate and the pentachloride are mixed in the proper proportions, and allowed to remain in contact at the ordinary temperature for some time, and finally slightly warmed; the quantity of phosphorus oxychloride formed is almost the theoretical amount; after distilling off in a vacuum, it boils entirely between 108° and 110°, and contains only traces of phosphorus trichloride. By agitating with petroleum (previously boiled over sodium for a long time) the phosphorus oxychloride is slowly washed away, and a crystalline mass left. This can be crystallised from petroleum boiling at 70°, in colourless, shining needles, melting at 71—72°; it is very difficult, however, to obtain the body, even approximately pure, as in contact with moisture, or on warming it loses the elements of hydrochloric acid, forming *phenylimido-mono-chloracetate of ethyl*, $\begin{array}{c} \text{OCl=N.C}_6\text{H}_5 \\ | \\ \text{CO.O.C}_2\text{H}_5 \end{array}$.

This latter body is readily obtained by crystallising from petroleum the residue left on distilling in a vacuum, and subsequently keeping at above 70° for some time, the product of the action of pentachloride of phosphorus on ethyl phenyloxamate. It melts at 91°; it may also be obtained by passing ammonia-gas into a solution of phenylamido-dichloroacetic ether in benzene, sal ammoniac being simultaneously formed. In contact with moisture, it rapidly forms hydrochloric acid and ethyl phenyloxamate; alkalis act similarly, the ethyl phenyloxamate being further saponified; ammonia forms monophenyloxamide,

and aniline gives rise to a product, $\begin{array}{c} \text{NH.C}_6\text{H}_5 \\ \diagdown \\ \text{O=N.C}_6\text{H}_5 \\ | \\ \text{CO.NH.C}_6\text{H}_5 \end{array}$, belonging to the

same class of bodies as Strecker's acediamine; this melts at 234—235°; a little oxanilide is simultaneously produced. When boiled with alcohol or water, this new substance splits up, forming aniline and oxanilide, thus:—



No definite substances could be extracted from the residue left on heating 20 grams of phenylamidodichloracetate of ethyl to 123—

130° for three hours; no basic bodies were obtained analogous to those prepared by Wallach from diethyloxamide. In order to decide whether this is due to the influence of the benzene group, the author examined the *paratolyloxamethane* obtained from toluidine and oxalic ether by a reaction parallel to that above described: the results in this case also were negative. The paratolyl-oxamethane employed melted at 66—67°, after repeated crystallisation from dilute alcohol; with caustic potash it formed potassium paratolyloxamate, from which

$\text{CO.NH.C}_6\text{H}_4.\text{CH}_3$
paratolyloxamic acid, $\left| \begin{array}{l} \text{CO.OH} \end{array} \right.$, was prepared by the action of

hydrochloric acid; this melted at 168—170°, and formed barium and calcium salts, much resembling those of phenyloxamic acid. When the paratolyloxamethane was heated with phosphorus pentachloride, it readily formed phosphorus oxychloride and *paratolylamido-dichloro-*

$\text{CCl}_2.\text{NH.C}_6\text{H}_4.\text{CH}_3$
acetate of ethyl, $\left| \begin{array}{l} \text{CO.O.C}_2\text{H}_5 \end{array} \right.$, melting at 59—60°; from this

paratolyloxamic ether is reproduced on boiling with water, whilst aniline forms a body resembling the complex substances similarly formed from phenylamidodichloracetate of ethyl.

It results from these experiments and those of Gerhardt and of Wallach, that phosphorus pentachloride acts on amides in accordance with the equation—



the resulting dichlorinated body readily losing the elements of hydrochloric acid, forming a monochlorinated imide.



Both the di- and the monochlorinated bodies act alike with water, alkalis, and aniline; if, however, R be a radicle derived from the benzene family (phenyl or paratolyl) they do not form basic bodies analogous to the chloroxaethyline of Wallach. C. R. A. W.

Preliminary Note on Naphthalene Derivatives. By J. GUARESCHI (*Gazzetta chimica italiana*, vii, 24—25).—Nitronaphthalene, in whatever manner prepared, is always identical in properties, melting at 58.5° to 59°. When oxidised with potassium permanganate, it yields nitrophthalic acid, fusing at 208—210°, besides another acid, and a small quantity of a substance which melts at 154°, and crystallises in regular octohedrons, possibly identical with Lossen's dinaphthyl (C_{16}H_7)₂.

The two dibromonaphthalenes prepared by Glaser's method are easily separated by crystallisation. The α -compound treated with nitric acid, yields Laurent's bromodinitronaphthalene, and a bromophthalic acid melting at 135°; this is at the same time decomposed into carbonic anhydride, and a magnificently crystallisable anhydride, which melts at 207.5—208°. Of the five dibromonaphthalenes, which

have been described, the author believes that two are impure forms of some of the others.

The action of bromine on nitronaphthalene does not easily cause displacement of the NO_2 group, as usually stated, the first products being bromonitronaphthalenes, one of which melts at 122° , the other at about 100° . Even by heating at 100° with excess of bromine, it is difficult to convert these nitro-derivatives into dibromonaphthalene; the author believes, however, that the product is identical with Glaser's α -modification, which melts at 81° . C. E. G.

Herapathite and similar Acid Periodides. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], xiv, 356—387). (Continuation, see this Journal, clxx, 210).—D. QUINIDINE COMPOUNDS. By quinidine is meant the quinidine of Pasteur and the conchicine of Hesse. 1st. *Quinidine-sulphato-periodide*, $2\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{SH}_2\text{O}_4 \cdot 2\text{HI} \cdot \text{I}_2$. Prepared by dissolving quinidine in the theoretical quantity of normal sulphuric acid and hot alcohol, and adding the calculated quantity of hydriodic acid, and a little less than the required quantity of iodine in hot alcoholic solution. It consists of red needles with a bluish lustre, which scarcely absorb polarised light, and are very brilliant. When heated to 100° , they decrepitate strongly on cooling, which shows that they are anhydrous.

2nd. *Quinidine Sulphatoperiodide*, $3\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot 3\text{SH}_2\text{O}_4 \cdot 2\text{HI} \cdot \text{I}_2$, is difficult to prepare. The best results were obtained with 3.5 grams of quinidine (containing 8 to 10 per cent. of water), 25 c.cm. dilute sulphuric acid (17 per cent. of SO_3) and 60 c.cm. of alcohol (92 per cent.), to which were added 2 grams of iodine in 60 c.cm. of alcohol (92 per cent.). The iodine solution must not be heated to more than 50° , and the acid liquid should not have a much higher temperature. This compound consists of olive brown rhombic plates, or small flattened prisms. It appears to undergo a peculiar change on keeping; the free iodine becoming less, although the total amount does not perceptibly diminish. This compound easily passes into the foregoing one, but the two do not, as Herapath supposed, contain different modifications of quinidine. Bisulphide of carbon is scarcely coloured by the second sulphatoperiodide in the cold, but faintly when hot. Chloroform and ether are not affected by it. It is soluble in hot alcohol, and on slow cooling the solution deposits a reddish-brown powder, together with brilliant brown prisms, very much like the first sulphatoperiodide. These crystals, however, consist of a totally different compound.

E. ETHYL-QUINIDINE COMPOUND.—When an alcoholic solution of quinidine is mixed with ethyl iodide and excess of ether, colourless silky needles of ethyl-quinidine iodide are deposited. A solution of the neutral chloride may be obtained by digesting the iodide with silver chloride and water. This chloride is not precipitated by caustic soda or ammonia, or the alkaline carbonates. *Platinum chloride* throws down an orange-coloured almost insoluble double salt consisting of very small crystals. From a highly dilute boiling solution strongly acidified with hydrochloric acid, larger crystals may be obtained. *Gold chloride* produces a yellow precipitate, partly soluble on heating, partly however forming a brownish-yellow oil. The freshly precipi-

tated salt is soluble in alcohol. *Mercuric chloride* gives a white almost insoluble precipitate, melting on application of heat into a colourless oil. The precipitate formed in the cold is easily soluble in warm dilute hydrochloric acid, and colourless needles are deposited on cooling. *Iodide of potassium and mercury* gives a white bulky precipitate: yellow needles separate from a hot alcoholic solution. *Bismuth iodide* throws down from a cold aqueous or a hot alcoholic solution a scarlet, amorphous precipitate. *Potassium iodide* gives a precipitate soluble with difficulty in cold water, but easily soluble in hot water. The iodide crystallises on cooling in beautiful silky, doubly-refracting needles. The *tri-iodide* is formed in hot alcoholic solutions on addition of potassium periodide, in the form of long brown needles. *Potassium sulphocyanate* gives a bulky, white, crystalline precipitate soluble in hot water, and crystallising in brilliant doubly refracting needles. *Potassium chromate* gives no precipitate, but the bichromate throws down a bulky yellow one. Acid silver sulphate gives a strongly fluorescent filtrate.

Ethyl-quinidine Sulphatoperiodide, $2C_{20}H_{24}N_2O_5(C_2H_5)_2I.S_2H_2O_4.I_4$.—If two molecules of ethyl-quinidine iodide and one of sulphuric acid are mixed with hot alcohol (93 per cent.), and four atoms of iodine dissolved in warm alcohol are added, the acid periodide crystallises out on cooling, in dark brown prisms having a metallic lustre. This compound is very similar in appearance to No. 1. It dissolves with difficulty in hot alcohol, and imparts no colour to chloroform, ether, or bisulphide of carbon. The double salt with mercury crystallises in bright yellow rhombic prisms. With nitrate of silver, iodate as well as iodide of silver is formed.

F. CINCHONINE COMPOUNDS. 1st. *Cinchonine sulphatoperiodide*, $8C_{20}H_{24}N_2O.6SH_2O_4.6HI.I_{10}.12H_2O$.—Two molecules of cinchonine, one of sulphuric acid and two of hydriodic acid are dissolved in hot alcohol and mixed with two atoms of iodine. The compound obtained is so easily decomposed that it must be washed with ice-cold strong alcohol, and at once dried by pressure and over sulphuric acid. It begins to lose water at 70° , melts at 140 — 145° , and is perfectly decomposed at 170° with formation of chinoline. It is easily soluble in hot alcohol, but is not affected by ether, chloroform, and bisulphide of carbon. It forms a double salt with mercuric iodide.

2nd. *Cinchonine Sulphatoperiodide*, $4C_{20}H_{24}N_2O.2SH_2O_4.4HI.I_{10}$, is obtained by dissolving cinchonine in boiling alcohol, with addition of the calculated quantity of sulphuric acid and hydriodic acid, and for each molecule of cinchonine at the most 2 atoms of iodine. Attempts to recrystallise this body produce a mixture of the previous and the following compounds; possibly also cinchonine tri-iodide is formed at the same time. Ether and bisulphide of carbon are both slightly coloured by this compound when hot: chloroform is not affected by it. An alcoholic solution gives with mercury a subiodide and a double iodide.

3rd. *Cinchonine Sulphatoperiodide*, $2C_{20}H_{24}N_2O.SH_2O_4.2HI.I_8$, is probably identical with the cinchonine salt obtained by Herapath, and may be prepared in several ways, e.g., by dissolving the theoretical quantities of the constituents in hot alcohol, and precipitating by addi-

tion of water. This compound is slightly soluble in ether, bisulphide of carbon or chloroform, but dissolves with tolerable ease in hot alcohol. It behaves like the previous compound with mercury, thallium and silver. It contains unaltered cinchonine.

G. CINCHONIDINE COMPOUNDS.—By cinchonidine is meant the cinchonidine of Pasteur and the quinidine of Hesse.

1st. *Cinchonidine Sulphatoperiodide*, $12C_{20}H_{24}N_2O \cdot 9SH_2O_4 \cdot 8HI \cdot I_{12} \cdot 8H_2O$.—This compound (Herapath's brass-yellow salt) is easily prepared by slowly cooling a solution of the theoretical quantities of its constituents in hot alcohol. It crystallises in very fine rhombic golden plates. Bisulphide of carbon is only faintly coloured by it even when hot: ether and chloroform not at all. With mercury it gives mercurous iodide, and a double iodide. It is soluble in hot alcohol.

2nd. *Cinchonidine Sulphatoperiodide*, $4C_{20}H_{24}N_2O \cdot 2SH_2O_4 \cdot 3HI \cdot I_4 \cdot 4H_2O$, almost always separates from the mother-liquor of the previous and following compounds in long thin silky reddish-yellow or golden-yellow needles. When pure it loses all its water on drying over sulphuric acid. It imparts no colour to ether, chloroform, or bisulphide of carbon, but is soluble in hot alcohol. The solution forms no mercurous iodide when shaken up with mercury, but an almost white double salt crystallises out on cooling in silky faintly yellow stellate masses of flat needles. On dissolving it at a gentle heat in alcohol with addition of a very little sulphuric acid, a yellowish salt separates out on cooling, and afterwards an olive-green compound into which the whole is finally converted.

3rd. *Cinchonidine Sulphatoperiodide*, $8C_{20}H_{24}N_2O \cdot 5SH_2O_4 \cdot 6HI \cdot I_{12} \cdot 6H_2O$, may be prepared by dissolving 3.08 grams of cinchonidine in 100 c.cm. of alcohol (98 per cent.) and adding 10 c.cm. of sulphuric acid and 10 of hydriodic acid. If 1.905 grams of iodine in 50 c.cm. of alcohol are then added, and the temperature is kept at 55° , thin olive-green needles are formed, which must be filtered off before the liquid has cooled to below 30° . This periodide is not the same as the green compound described by Herapath. It has no effect on ether, chloroform, and bisulphide of carbon; it gives a double iodide with mercury, but no mercurous iodide is formed.

4th. *Cinchonidine-sulphatoperiodide*, $2C_{20}H_{24}N_2O \cdot SH_2O_4 \cdot HI \cdot I_4 \cdot H_2O$, is obtained by cooling a solution containing the calculated quantities of the constituents in hot alcohol. It consists of reddish or dark brown stellate masses of short thick, brilliant needles. It gives no colour to ether, chloroform, or bisulphide of carbon. With mercury it forms mercurous iodide and a double iodide. It is easily convertible by addition of hydriodic acid and dilution with water into the 2nd compound. Heated to 100° , and boiled with alcohol, it yields for the most part olive-green needles of the 3rd compound.

H. SULPHATO-PERIODIDES OF UNIVALENT BASES. *Aniline Sulphatoperiodide*, $6C_6H_7N \cdot 3SH_2O_4 \cdot HI \cdot I_4$, is prepared by mixing 6 molecules of aniline (in grams) in 6 to 7 molecules of sulphuric acid and 200 c.cm. of water, warming the mixture to $30-40^\circ$, and adding a solution of 4 atoms of iodine in one molecule of hydriodic acid and 50 c.cm. of alcohol. It must be washed with weak alcohol, dried by pressure between filter paper, and over sulphuric acid in the dark. This compound is

of a metallic green colour in large masses. It crystallises in rhombic plates, which polarise light but faintly if at all. By transmitted light the crystals appear of a fine bright reddish-brown, with a peculiar characteristic shade. The compound contains unaltered aniline. It is somewhat soluble in water, and the solution leaves a thin layer on evaporation such as the rosaniline salts do, of a metallic green by reflected, red by transmitted light.

It is decolorised when boiled with water: dissolves in alcohol (93 per cent.), and is scarcely affected by ether, chloroform and bisulphide of carbon. On shaking it up with mercury and hot alcohol, abundance of mercurous iodide is formed, and the filtrate contains a double salt with mercuric iodide.

Toluidine Sulphatoperiodide, $6C_7H_5N \cdot 3SH_2O_4 \cdot HI \cdot I_4$. — Paratoluidine forms a sulphatoperiodide strongly resembling the aniline compound. Several other compounds may also be obtained. Aniline for instance forms one with nitric acid in place of sulphuric acid; but they are all so prone to decomposition that they have not been satisfactorily analysed. Toluidine-phosphatoperiodide exhibits peculiar optical properties. G. T. A.

Improved Method of obtaining Nicotine, Conine, and Sparteine. By W. KIRCHMANN (*Arch. Pharm.* [3], ix, 209—210).—The tobacco or other material is placed in a vessel fitted with two tubes, one leading to the bottom and connected with an apparatus for generating carbon dioxide, and the other just passing into the vessel and leading to a receiver containing a mixture of alcohol and dilute sulphuric acid. The vessel containing the tobacco is heated in a steam-bath, and a strong current of carbon dioxide passed through, the volatilised alkaloids being condensed by the sulphuric acid. The alcoholic solution is diluted with water, decomposed by barium hydrate, and the nicotine taken up with ether. It is purified as usual.

E. N.

On the so-called Resina Gualacæ Peruviana Aromatica v. Odorata. By ADOLF KOPP (*Arch. Pharm.* [3], ix, 193—205).—The resin examined was of unknown origin, and at least 15 years old. It consisted of yellow brittle masses melting at 90° , and possessing a sharp disagreeable taste and a strong odour resembling that of rue or aniseed. It was readily soluble in hot alcohol, ether, chloroform, and carbon disulphide. The powdered resin on being distilled with water yielded 4 per cent. of a yellow ethereal oil with an odour like that of peppermint. On fractionation no fixed boiling point could be obtained, and the oil appeared to be a complex mixture. The fraction of lower boiling point boiled between 173° — 176° , had a specific gravity of 0.851, a rotation for polarised light of $+84.4$, and contained 84.29 per cent. of carbon and 11.64 per cent. of hydrogen. By repeated rectification over sodium a colourless oil was obtained boiling at 168° , and having the composition $C_{10}H_{18}$. The highest-boiling fraction boiled between 265° — 280° , had a specific gravity of 0.936, a rotation for polarised light of -17.2 , and contained 83.46 per cent. of carbon and 10.98 per cent. of hydrogen. The powdered resin on being fused

with potassium hydrate yielded protocathechuic acid. Boiling nitric acid dissolves the resin, and on dilution a yellow nitro-product separates: this compound readily forms neutral non-crystallisable alkaline salt. On analysis it gave numbers agreeing with the formula $C_{23}H_{34}N_2O_{10}$. By prolonged boiling with nitric acid the resin yields oxalic acid.

On dry distillation the resin gives a yellow oil, lighter than water, which on fractionation was found to have no fixed boiling point. The portion coming over below 193° is a light yellowish oil, turning red with alkalis and green with ferric chloride. The portions boiling between 193 — 210° are darker in colour, and give no crystalline compound with anhydrous hydrochloric acid. The fraction boiling between 255 and 270° has a splendid deep azure-blue in colour, and after repeated rectification boils between 285° — 290° , and gives numbers agreeing with the formula $C_{26}H_{30}O$. On rectification over sodium a colourless oil was obtained boiling between 250 — 270° , and of the composition $C_{20}H_{30}$. This blue oil appears to be of the same composition, and possesses the same properties as that obtained by Mössner from galbanum (*Ann. Chem. Pharm.*, cxix, 262). E. N.

Ostruthin. By E. v. GORUP-BESANZ (*Liebig's Annalen*, clxxxiii, 321—343).—Ostruthin is a new crystalline body obtained by the author from the root of *Imperatoria Ostruthium* (masterwort). The young root is digested with warm alcohol, the extract slowly evaporated over a water-bath, and the brown residue extracted with a mixture of 3 parts of ether and 1 part of ligroin of low boiling point. To the resulting solution ligroin is added as long as a brown precipitate falls, and the clear liquid is left to crystallise by spontaneous evaporation. By repeated treatment in this manner ostruthin is obtained in the pure state. From its ethereal solution ostruthin crystallises in dense white crystals belonging to the triclinic system. They melt at 115° , and resolidify at 91° to a yellowish waxy mass. Ostruthin is odourless, almost tasteless, and easily reduced to a white powder. On heating, it melts to a brown oil. It is insoluble in cold water, slightly soluble in hot water, benzene, and petroleum, and easily soluble in alcohol and ether. The alcoholic solution exhibits a faint sky-blue fluorescence, which on the addition of a small quantity of water becomes a magnificent blue, surpassed only by aesculin.

Ostruthin does not contain nitrogen, and the mean of eight analyses gave carbon 77.07 per cent., hydrogen 7.98 per cent., corresponding with the formula $C_{14}H_{17}O_2$, which requires carbon 77.42 per cent., hydrogen 7.83 per cent. Ostruthin is dissolved by dilute potash and by aqueous ammonia, forming fluorescent solution. Its alcoholic solution gives no precipitates with alcoholic solutions of lead acetate, mercuric chloride, silver nitrate, or ferric chloride.

Ostruthin hydrochloride, $C_{14}H_{17}O_2.HCl$, is formed by saturating with hydrochloric acid gas a moderately concentrated alcoholic solution of ostruthin. On concentrating the solution, the crude hydrochloride crystallises out, and may be purified by washing with water and recrystallising from ether. Ostruthin hydrochloride forms short slender needles without odour or taste, and melting at 100° to a yellow oil,

which solidifies to a waxy mass. It is insoluble in cold water, easily soluble in alcohol, ether, benzene, and chloroform, but less soluble in petroleum. Its solutions are completely neutral, and yield a precipitate of silver chloride when added to a solution of silver nitrate, and are decomposed by alkalis, which separate the hydrochloric acid.

Ostruthin hydrobromide, $C_{14}H_{17}O_2 \cdot HBr$, is obtained in a similar manner, and forms a similar body to the hydrochloride, only it is more easily decomposed.

Acetylostruthin, $C_{14}H_{18}(C_2H_3O)_2O_2$, is formed by dissolving ostruthin in acetic anhydride by the aid of a gentle heat, when, on cooling and standing, crystals of the new body separate out. Acetylostruthin crystallises in pearly glittering laminae, which melt at 78° , and re-solidify between 40° and 50° . It is not soluble either in cold or in boiling water, but dissolves easily in cold and hot alcohol, ether, benzene, and chloroform. It is decomposed by alkalis.

Benzoylostruthin appears to be formed by treating ostruthin with benzoyl chloride, but is not a crystalline body. When ostruthin is added to fused potassium hydrate, it is decomposed, and in the volatile products of the reaction acetic and butyric acids are found, whilst the residue contains resorcin. By the prolonged action of nitric acid, ostruthin yields oxalic and styphnic acids (trinitro-resorcin). Chlorine gas passed over heated ostruthin yields hydrochloric acid and a chlorinated compound. Bromine in like manner yields hydrobromic acid and an oily body. This last dissolves in alcohol, and the solution yields minute yellowish crystals of *tetrabromostruthin*, $C_{14}H_{13}Br_4O_2$. From the mother-liquor a pale yellow powder can be separated, consisting of *tribromostruthin*, $C_{14}H_{14}Br_3O_2$, mixed with a little tetrabromostruthin.
E. N.

Picrorocellin. By J. STENHOUSE and C. E. GROVES (*Proc. Roy. Soc.*, 60—68).—Picrorocellin, $C_{27}H_{32}N_2O_6$, is a bitter crystalline substance, occurring in a variety of *Rocella fuciformis* growing on limestone rocks, and believed to have been brought from the West Coast of Africa. It was extracted from the lichen by boiling it with spirit, after the erythrin had been removed by hydrate of lime and water, or by dilute ammonia. On distilling off the spirit, a dark green pasty mass was left, which was purified by washing with a small quantity of boiling spirit and with benzene, and then recrystallised from boiling spirit. By this means a mixture of two substances was obtained, one crystallising in lustrous prisms, and the other in feathery tufts of minute flattened needles. These could easily be separated mechanically by elutriation, and the large prisms of picrorocellin finally purified by two or three crystallisations from alcohol. It forms long prismatic crystals which are almost insoluble in water, but moderately soluble in boiling spirit. It melts at 192 — 194° , and at a higher temperature boils and gives off vapours of an oily substance of pleasant aromatic odour, leaving a small amount of carbonaceous residue. When distilled with dilute sulphuric acid and potassium dichromate, it is decomposed, benzoic acid and an oil having the odour of benzoic aldehyde passing over. When boiled with dilute sulphuric or hydrochloric acid for a short time, picrorocellin is changed into *wantho-*

rocellin, a substance which crystallises from its alcoholic solution in long silky needles of a pale yellow colour. The most convenient method of preparation is to boil a solution of picrorocellin in glacial acetic acid with a few drops of hydrochloric acid for a short time, precipitate with water, wash, and recrystallise from spirit. The same substance is formed when picrorocellin is heated at 220° for about ten minutes.

Xanthorocellin, $C_{21}H_{17}N_2O_3$, is insoluble in water, but readily soluble in boiling spirit. It melts at 183° , and when treated with nitric acid gives rise to benzoic aldehyde and two crystalline nitro-derivatives, which have not as yet been further examined.

When picrorocellin is boiled with a dilute solution of sodium hydrate, it dissolves, and a little ammonia is given off. The addition of an acid to the clear solution causes a precipitate which in the warm liquid agglutinates to a plastic mass. This, when crystallised once or twice from alcohol and from carbon bisulphide, yields a colourless crystalline substance in large brilliant prisms having the formula $C_{24}H_{22}N_2O_3$. It is very soluble in alcohol, but only very slightly in ether. It melts at 154° , and when boiled with dilute acids it yields xanthorocellin. Oxidising agents give rise to benzoic aldehyde and benzoic acid.

As it possesses an exceedingly bitter taste, and is moreover a nitrogenous compound, it was thought probable it might possess medicinal properties. Dr. T. Lauder Brunton examined it with this object, but the results obtained were negative.

C. E. G.

Picrotoxin. By E. PATERNÒ and A. OGLIALORO (*Gazzetta chimica italiana*, vi, 531—534).—The chemical constitution of this substance is completely unknown, and even the formula is uncertain, that of Barth, $C_{12}H_{14}O_5$, being generally accepted however, from the evidence afforded by the dibromide, $C_{12}H_{12}Br_2O_5$, and mononitrate, $C_{12}H_{13}(NO_2)O_5$, prepared and analysed by that chemist. The authors, notwithstanding, began by analysing a specimen of picrotoxin, the purity of which was guaranteed by the melting point remaining constant at 199 — 200° , even after repeated fractional crystallisation. The results of five concordant analyses, made with various specimens dried in a vacuum at the ordinary temperature, at 100° and at 130° , agree very nearly with the formula $C_9H_{10}O_4$, which requires 59.34 per cent. carbon, and 5.49 hydrogen, whilst the formula $C_{12}H_{14}O_5$ requires 60.50 C. and 5.88 H. If the formula $C_9H_{10}O_4$ is correct, picrotoxin is isomeric with veratric, hydrocaffeic, and evernic acids. Attempts were made to obtain the dibromopicrotoxin of Barth by acting on picrotoxin in ethereal solution with bromine. An unstable crystalline mass was obtained, similar to that described by Barth, but after being washed with alcohol and ether, it contained only 21.39 per cent. of bromine, whilst the formula $C_{12}H_{12}Br_2O_5$ requires 40 per cent. When this substance is dissolved in boiling alcohol, and the solution allowed to cool, it deposits long needles, which are much less soluble in alcohol than picrotoxin, and do not melt at 240° , but decompose completely at 253° . It is free from bromine.

On passing dry hydrochloric acid into an ethereal solution of picrotoxin, a crystalline substance is gradually deposited, which is insoluble

in most solvents. It melts without decomposition at a temperature above 310° . The analytical results lead to the formula $C_{27}H_{28}O_{11} = 3(C_9H_{10}O_4) - H_2O$. The same substance, *picrotoxinide*, is produced by the action of acetyl chloride, and probably by other dehydrating agents. The authors are continuing their researches on the derivatives of picrotoxin.

C. E. G.

The Insoluble Matter from Opium Extract. By PERIER (*Chem. Centr.*, 1876, 248).—50 grams of opium extract dissolved in 500 grams of water yielded 1.312 grams of insoluble matter, which contained 0.024 gram of morphine and 0.008 gram of other crystalline matter. The residue is soluble in a concentrated solution of the extract itself.

M. M. P. M.

The Constituents of Balsam of Tolu. (*Pharm. J. Trans.* [3], vii, 354).—The ethereal extract of tolu balsam yields on distillation benzyl benzoate ($C_{14}H_{12}O_2$), benzyl cinnamate ($C_{15}H_{14}O_2$), and a liquid which passes over first, and appears to be impure benzyl alcohol. Balsam of Tolu, therefore, contains the same constituents as balsam of Peru—a fact which had long been disputed; but cinnamic acid predominates in the former, benzoic acid in the latter. If the ethereal solution be first treated with soda, cinnamic and benzoic acids are obtained, so that these acids are present as well as their ethers.

E. W. P.

Note on Capsaicin. By J. C. THRESH (*Pharm. J. Trans.* [3], vii, 473).—Crude capsaicin may be purified by dissolving it in potash, precipitating with carbonic anhydride, crystallising from petroleum, and recrystallising from dilute alcohol. The product thus obtained has the formula $C_8H_{14}O_2$.

E. W. P.

Preliminary Note on Xanthium Spinosum. By GUICHARD (*Pharm. J. Trans.* [3], vii, 249).—The alcoholic and aqueous extracts of the above plant were compared, and it was found that when the alcoholic extract was dissolved in water, it was precipitated by iodized potassium iodide, but not by cadmi-potassium iodide. This aqueous extract, when dried and treated with ether, yielded precipitates with both the above iodides, and crystallised in star-shaped groups of needles. From the solution in hydrochloric acid, rectangular tables and acicular crystals are deposited.

The aqueous extract, treated in the same manner, gave no results.

E. W. P.

Chemistry of the Barks of the Oak, Willow, and Elm. By E. JOHANSEN (*Arch. Pharm.* [3], ix, 210—248).—The investigation was undertaken with the view of ascertaining the nature of the different tannin-like substances contained in the barks of the oak, willow, and elm, and it was hoped, by isolating these and carefully examining their properties and the nature of their principal compounds, to ascertain whether they were analogous or even identical. By a long and

elaborate process, the different tannins were separated from the three barks in something like a pure state.

Oak Tannin is a red-brown amorphous glistening body, easily soluble in alcohol, slightly soluble in ether, and forms an imperfectly clear solution in water. In its behaviour to litmus paper, metallic salts, and alkaloids, it is completely analogous to gallotannic acid. Dried at 110° , it lost 8.48 per cent. of water. On analysis, it gave 54.61 per cent. of carbon, 5.32 per cent. of hydrogen, and 40.07 per cent. of oxygen, agreeing approximately with Wagner's formula, $C_{14}H_{16}O_8$, which requires 53.85 per cent. of carbon, and 5.13 per cent. of hydrogen. It contains also 0.77 per cent. of nitrogen and 0.13 per cent. of ash.

Willow Tannin consists of a brown-red amorphous body, with a slightly astringent taste; easily soluble in alcohol, slightly soluble in ether, and forming a thick solution with water. With ferric salts it gives a deep black colour, turned violet-red by alkalis. It precipitates mercuric nitrate and chloride, and zinc and copper sulphates, as well as albumin, starch, and alkaloids. At 120° the willow tannin lost 10.10 per cent. of water, and on analysis gave 51.13 per cent. of carbon, 4.78 per cent. of hydrogen, and 44.09 per cent. of oxygen. It contains also 1.88 per cent. of nitrogen and 1.63 per cent. of ash. Another specimen, prepared in a different manner, though possessing the same reactions as the last, contained 51.26 per cent. of carbon and 5.99 per cent. of hydrogen, besides having independently 0.44 per cent. of nitrogen and 1.42 per cent. of ash.

Elm Tannin.—In appearance and solubility this variety resembles oak tannin. With ferric chloride, it gives a dirty-green precipitate, turned violet-red by sodium hydrate. With ferrous sulphate, it gives a pure-green precipitate. It precipitates lead and copper acetates, and zinc sulphate after some time. With zinc chloride, mercuric nitrate, calcium acetate, &c., it gave the usual reactions. At 110° elm tannin loses 3.32 per cent. of water, and, on analysis, gives 44.54 per cent. of carbon, 4.72 per cent. of hydrogen, and 50.74 per cent. of oxygen, besides containing 1.21 per cent. of ash.

The salts of these three tannin acids (quercitannic, salitannic, and ulmotannic) were next examined.

Lead Salts.—Quercitannate of lead is a chocolate-brown, amorphous mass, slightly soluble in water, insoluble in alcohol or ether. On heating it to 110° , it lost 9.66 per cent. of water; and on analysis it gave 22.85 per cent. of carbon, 1.47 per cent. of hydrogen, 9.14 per cent. of oxygen, and 36.54 per cent. of lead oxide. The salitannate of lead resembled the last body, and on drying at 120° lost 4.50 per cent. of water, and on analysis gave 22.53 per cent. of carbon, 1.35 per cent. of hydrogen, and 53.28 per cent. of lead oxide. By fractionally precipitating with a lead salt, both these acids gave salts of varying constitution. Ulmotannate of lead was greyer than the last body; and on analysis gave 21.36 per cent. of carbon, 1.51 per cent. of hydrogen, 10.32 per cent. of oxygen, and 66.81 per cent. of lead oxide.

Copper Salts.—Quercitannate of copper is a brown substance, insoluble in alcohol and ether, and sparingly soluble in water. At 110° it lost 12.23 per cent. of moisture, and on analysis gave 39.99

per cent. of carbon, 2·38 per cent. of hydrogen, 28·14 per cent. of oxygen, and 29·49 per cent. of copper oxide. Salitannate of copper forms a dark reddish-brown salt, which lost at 120° 12·4 per cent. of moisture; and on analysis gave 39·36 per cent. of carbon, 2·35 per cent. of hydrogen, 27·83 per cent. of oxygen, and 30·46 per cent. of copper oxide. Ulmotannate of copper is chocolate-brown, and after drying at 110° gave 39·68 per cent. of carbon, 1·93 per cent. of hydrogen, 17·98 per cent. of oxygen acid, and 40·41 per cent. of copper oxide.

Tin Salts.—Quercitannate of tin is a greenish-brown substance, insoluble in alcohol and ether, and only sparingly soluble in water. At 110° it loses 5·98 per cent. of moisture, and on analysis gave 36·32 per cent. of carbon, 2·56 per cent. of hydrogen, 20·69 per cent. of oxygen, and 40·43 per cent. of stannous oxide. The formula $C_{30}H_{26}O_{13} \cdot 3SnO$ agrees fairly with these numbers. Salitannate of tin is a chocolate-coloured body, which loses 7·18 per cent. of moisture at 120°, and on analysis gives 35·17 per cent. of carbon, 2·79 per cent. of hydrogen, 15·05 per cent. of oxygen, and 46·50 per cent. of stannous oxide. Ulmotannate of tin on drying at 110° gave 38·99 per cent. of carbon, 2·40 per cent. of hydrogen, 13·66 per cent. of oxygen, and 44·95 per cent. of stannous oxide.

When these different tannins were acted on by dilute acids in the usual manner, as Grabowski has already shown, the oak tannin yields an easily decomposed saccharide and a crystalline body. The amount of these bodies obtained varies with the strength of acid employed. On purification the saccharide is obtained as a brown substance, forming a dark-brown bitter syrup. Similar bodies were obtained from the willow tannin. On analyses the saccharide obtained from the willow tannin gave 36·94 per cent. of carbon, 5·19 per cent. of hydrogen, and 57·87 per cent. of oxygen. Elm tannin, on the contrary, yields no crystalline body, but only a saccharide resembling in every respect the last.

On fusing with potassium hydrate, the oak tannin yields, amongst other products, butyric acid amongst the volatile products, and protocatechuic acid from the residue. Willow tannin, similarly treated, yielded acetic and butyric acid amongst the volatile products, whilst the residue in the retort contained a body whose identity could not be satisfactorily made out. Elm tannin, treated in the same manner, yielded acetic and butyric acids among the volatile products, and oxyphenic acid in the residue.

E. N.

Decomposition of Catharidin in Cantharides. By R. WOLFF (*Arch. Pharm.* [3], x, 22—30).—It is stated that, although the composition of the proximate constituents of cantharidin is not altered by the influence of chemical reagents, *e.g.*, by the action of concentrated sulphuric acid, this substance nevertheless loses its characteristic vesicating properties in cantharides; moreover, the fact that cantharides remain active for a long time when kept in a dry place, but lose their activity very quickly when exposed to moisture, cannot be regarded as being the essential cause of a conversion or decomposition of cantharidin, since the latter *per se* does not suffer by exposure to the air. It is evident, therefore, that cantharides must contain sub-

stances which, when assisted by moisture, effect a conversion of the cantharidin. To this effect the author undertook a complete series of experimental investigations, when the following reactions were obtained :—

The evolution of ammonia gas, which takes place on treating an aqueous extract of old cantharides with potash-ley, especially if the action is aided by heat, led to the idea that this gas plays an important part in the decomposition of cantharidin. The cantharides experimented on was the *Lytta aspersa*, which is largely used in America, and is distinguished from the European by its greater activity. The specimens used were more than two years old. 100 grams were powdered and exhausted with ether. The latter was distilled off, and the crystals which were separated from the oily residue were collected on a filter and washed with ether, until they showed only a faint yellow colour. After drying, the crystals of cantharidin weighed 0.815 gram. The oily substance from which the cantharidin had been separated was warmed with the ether used for washing the crystals, until the whole of the ether had been driven off. The residue was then saponified with potash-lye. By adding a solution of pure chloride of sodium, a soda-soap was deposited and removed by filtration. The liquor was evaporated on a water-bath, the residue re-dissolved in water, and the solution filtered, supersaturated with hydrochloric acid, and again evaporated. The residue was digested with ether, the extract evaporated, and the residual product treated with a small quantity of 80 per cent. alcohol, in which it dissolved very readily, with separation of a small quantity of cantharidin. The latter was thrown on a filter, washed with alcohol, dried and weighed: amount obtained, 0.04 gram. The cantharides exhausted by ether were then digested for 24 hours with cold distilled water, until the latter was colourless when filtered. The aqueous extract was evaporated to a syrupy mass, and treated with a solution of barium chloride, which produced a copious brown precipitate. The latter was filtered off, washed, and whilst wet transferred to a dish and evaporated to dryness, after addition of an excess of hydrochloric acid. The product thus obtained was an almost black mass, very hygroscopical, and difficult to pulverise. It was put into a small bottle containing chloroform, and digested for several days. The mixture was then filtered, and the residue insoluble in chloroform washed on a filter with chloroform, until the filtrate, when evaporated to dryness, no longer showed any traces of a crystalline residue. The chloroform was coloured yellowish, and gave on evaporation a yellowish-brown crystalline residue, which, when treated with a small quantity of ether, yielded white prismatic crystals, weighing 0.46 gram when dry. The ether used for purification appeared to have dissolved mere traces of the crystals. These crystals differ from cantharidin in form, and in some of their chemical properties, although they likewise exert a vesicating action. They are sparingly soluble in distilled water, at the ordinary temperature (1 : 6600), more readily in hot water, the solution depositing small granular crystals on cooling. Nitrate of silver does not precipitate the aqueous solution; chloride of barium gives a slight white precipitate, soluble in hydrochloric acid. Alcohol of 97 p. c. dissolves the crystals more readily than water

(1 : 680). By adding nitrate of silver to the alcoholic solution, an opalescence is produced, which disappears when nitric acid is added. Chloride of barium occasions a slight precipitate, readily soluble in hydrochloric acid. The crystals dissolve in ether, in the proportion of 1 : 390. They are most readily soluble in chloroform (1 : 60). Hydrochloric acid does not alter them, even on boiling. They are further soluble in concentrated nitric acid, and on boiling the solution a small portion seems to be converted into cantharidin and nitrate of ammonia. Concentrated sulphuric acid dissolves the crystals readily, with decomposition, cantharidin being separated by the addition of water, whilst sulphate of ammonia is formed simultaneously. 0.45 gram crystals gives 0.427 gram cantharidin. The crystals dissolve readily in acetic ether, the residue on evaporation consisting of cantharidin. The powdered crystals dissolve in potash-lye, at the ordinary temperature, more readily when warmed. On boiling this solution no indications of ammonia were perceived. The solution when evaporated to dryness and heated in a tube, turns black, evolving empyreumatic vapours, together with ammonia-gas. This potassium compound of the nitro-derivative of cantharidin crystallises with difficulty, and is hygroscopic. Its solution turns red litmus-paper blue; acids precipitate it in a crystalline form. The potash solution of this compound is precipitated by chloride of barium, the white precipitate formed being soluble in hydrochloric acid. Ferrous sulphate produces a white deposit, which assumes a reddish-yellow colour. Ferric chloride does not alter the solution, and forms a crystalline deposit of the compound after some time only. Nitrate of silver produces a white precipitate, soluble in nitric acid. Mercuric chloride forms a white precipitate. A solution of lead nitrate gives the same result. Solutions of magnesium salts, zinc, and copper salts, are not altered. The above mentioned cantharidin compound also dissolves in ammonia at the ordinary temperature. Acids reprecipitate the compound from this solution. By concentrating the solution crystals of the ammonia compound are obtained, which, when dried, are decomposed with evolution of ammonia. The crystals are then insoluble in water. By evaporating the solution of the ammonia compound to dryness on a water-bath, a white crystalline residue is obtained, which is insoluble in cold water, but readily soluble in hot water. On cooling needle-shaped crystals are separated. The following are the properties of these compounds :—(1.) The potash compound. (2.) The ammonia compound.

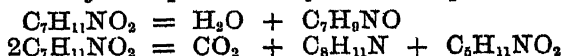
Compound (2) has a vesicating property. It is sparingly soluble in water, but dissolves readily in a larger quantity of hot water; sparingly soluble also in alcohol, ether, and chloroform, even when hot. It dissolves in acetic ether, leaving a residue of cantharidin when evaporated. An aqueous solution of compound (2) is not precipitated by salts of magnesium, zinc, copper, or iron. Chloride of barium produces a slight precipitate. Nitrate of lead or silver gives similar results. Mercuric chloride separates crystalline laminae, which, when dried, dissolve in boiling alcohol. The crystals of compound (2) are readily soluble in concentrated sulphuric acid, hydrochloric acid, and nitric acid, also in ammonia. Acids precipitate the latter solution,

forming needle-shaped crystals. Potash dissolves compound (2). The solution evolves ammonia when evaporated to dryness, while a portion of it is converted into compound (1). By fusing or subliming compound (2) no change takes place, but compound (1) melts with partial decomposition, the melt being partially soluble in chloroform. The insoluble portion is readily soluble in alcohol, and crystallises on evaporation in the form of crystalline fibres. The author thinks it probable that these crystals form another nitro-compound of cantharidin. By adding a zinc salt to a solution of cantharidin in potash until no further precipitation is observed, compound (1) is separated in the form of a white crystalline powder, if sufficient ammonia is first added, and then an excess of acid. Salts of copper and magnesia act in the same way. Since cantharides contain a large amount of magnesia salts, it may be supposed that, after the death of the animals, the latter, as ammonia gas begins to be evolved, occasion a conversion of cantharidin into compound (1). The fact that by using acetic ether for extracting the cantharidin a larger yield is obtained, is also explained from what has been stated.

In conclusion it is suggested that an accurate investigation of the nitrogen-compounds of cantharidin may be of great importance to chemists, in giving them means of re-obtaining the cantharidin decomposed in cantharides. The author strongly recommends the use of cantharidin preparations in the place of those of cantharides, as the former could be prepared more cheaply, while their action can always be depended upon. D. B.

New Derivative of Albuminoid Substances. By P. SCHÜTZENBERGER (*Compt. rend.*, lxxxiv, 124—126).—The liquid resulting from the action on albumin of solution of baryta at 130° was precipitated by carbonic acid, filtered and concentrated. Crystals, formed chiefly of leucine, tyrosine and butalanine were deposited, and the mother-liquid, after dilution, complete removal of remaining baryta by sulphuric acid, filtration, and concentration, yielded several fresh crops of crystals. From the first of these the substance in question was isolated by repeated fractional crystallisation. It is white, chalky-looking, crystallising in larger or smaller balls. It is soluble in water, scarcely so in cold alcohol, and not at all in ether. When distilled, it fuses at 250°, and splits up into: first, water and the carbonate of a volatile base, these forming together in the receiver a thick liquid interspersed with crystalline plates; second, a white sublimate; third, a residue of yellow liquid which congeals on cooling. The distillate has a smell and taste reminding one of horse-radish, and fumes strongly on the approach of a glass rod dipped in hydrochloric acid. It yields not the least trace of tyrosin. Its analysis corresponds with the formula, $C_7H_{11}NO_2$, and when neutralised with hydrochloric acid it gives with platinic chloride, an abundant yellow crystalline precipitate, having the composition $PtCl_4 \cdot 2(C_7H_{11}NO_2)$. The odour of horse-radish was found to be due to an oily base in the distillate, which base appeared to have the same composition as colidine, but will be the subject of further examination by the author. The sublimate has the characters of butalanine. The fusible residue

in the retort is insoluble in water and in alcohol, and has the composition C_7H_9NO . According to these results, the pyrogenous reaction above described may be represented by the two equations:—



The author proposes for the new amidated compound the name *tyroleucine*. R. R.

Physiological Chemistry.

Coagulation of Fibrin. By A. SCHMIDT (*Compt. rend.*, lxxxiv, 112—115).—In order to obtain in a pure state the substance which he terms a *ferment*, the author proceeds as follows:—Blood serum is coagulated by the addition of 20 times its volume of alcohol; the mixture after standing for four weeks is filtered; and the clot, after drying at ordinary temperatures, is powdered and exhausted with water. The filtered solution contains the ferment, some traces of salts, and a minute quantity of fibrinoplastic substances which have passed through the filter. These last may be removed by precipitation with carbonic acid, and prolonged treatment of the clot with alcohol.

Certain serous exudations, and those liquids which spontaneously coagulate in the animal economy, under normal circumstances, the author terms *proplastic* liquids. Such a liquid may be obtained from the fresh-drawn blood of a horse by mixing it with magnesium sulphate and filtering the plasma, which, when mixed with much water, does not coagulate, or at least does not do so completely, even after fully eight hours' standing. When, however, such a liquid is mixed with the solution of the ferment, coagulation takes place in a few minutes, or in a few hours, according to the quantity of ferment employed.

There are other serous exudations distinguished by their perfect limpidity, which contain no fibrinoplastic substances, but fibrin-producing substances only. Of these, called by the author *fibrogens*, the pericardial fluid of the horse is an example. The solution of the *ferment* free from fibrinoplastic substances is without action on fibrogens, but blood-serum causes their coagulation. A fibrogenous liquid is not acted on either by the ferment or by fibrinoplastic matter (which is readily obtainable from white of egg) when used alone, but when these two substances are added simultaneously, coagulation is produced. R. R.

Contributions to the Theory of the Coagulation of Fibrin. By OLOF HAMMARSTEN (*Pflüger's Archiv. f. Physiologie*, xiv, 211—273).—The author contends, in opposition to Alexander Schmidt, that paraglobulin does not unite with fibrinogen to form fibrin, nor become in any way converted into fibrin. He considers that for coagulation only an albuminous body, fibrinogen, is necessary. The

author concludes—(1) that paraglobulin is not absolutely necessary for coagulation; (2) that the mutual relation between the two globulins, assumed by Schmidt to be necessary, does not exist; and, finally, that paraglobulin does not pass over into fibrin.

Under the heading of "*Preparation of pure Fibrinogen*," the author defends at length his method against the objections made to it by Schmidt. The method is as follows:—Horse blood is received into one-fourth its volume of a saturated solution of sulphate of magnesia, and the corpuscles having been separated from the plasma by filtration, the latter is mixed with an equal volume of a saturated solution of sodium chloride. The deposit is then pressed between paper, and dissolved in a 6 to 8 per cent. solution of sodium chloride; again precipitated by an equal volume of a saturated solution of sodium chloride, expressed, and dissolved in a 6 to 8 per cent. solution of the same salt, and so on. That the solution of fibrinogen thus obtained can contain no typical unchanged paraglobulin (Schmidt's fibrinoplastic substance) is proved on the one hand, the author considers, by his previous researches, and on the other by those of Schmidt on the transformation of paraglobulin. Fourfold precipitation, as described above, appears to guard against the presence of changed paraglobulin, for by this means paraglobulin, according to Schmidt, is rendered insoluble; and paraglobulin thus rendered insoluble is, moreover, according to the same observer, fibrinoplastically inert.

2. *On the Action of Chloride of Calcium, impure Casein, and Neutralisation on the Coagulation*.—The author asserts that he has obtained the same results by other means as are obtained by paraglobulin. These results are, according to Schmidt—(1) an increase of the fibrin by the addition of paraglobulin; (2) the production of coagulation by the addition of paraglobulin and a solution of ferment in fluids which do not coagulate on the addition of ferment only. Not being able to prove for certain that his casein deposits are quite free from paraglobulin, the author prefers to disregard these experiments for the present, and relies only on those with chloride of calcium and neutralisation. In them he obtains by these reagents results similar to those produced by paraglobulin on a non-coagulating mixture of a solution of ferment and transudation.

3. *On the Mode in which Paraglobulin acts in Coagulation*.—The author does not consider it possible at present to give a satisfactory explanation of the mode of action of paraglobulin in coagulation, but proposes the following theory. In all natural solutions of fibrinogen can be demonstrated the presence of bodies hindering the coagulation. These act not only on the ferment, but also on the fibrin, by dissolving it, and dissolving probably with even more facility what the author terms "soluble fibrin," i.e., the intermediate product between fibrinogen and fibrin. These bodies are, he considers, the alkalis and neutral salts. Paraglobulin, according to the author, exerts an influence on the quantity of fibrin formed—(1) by means of the ferment, which is always adherent to the paraglobulin; and (2) by its affinity to the fibrin-dissolving substances. By this affinity it would, as it were, appropriate the fibrin-dissolving bodies to itself, and thus increase the quantity of fibrin deposited.

Our knowledge of the nature and conditions of coagulation will, the author thinks, be best advanced by endeavours to obtain pure, as far as possible, the substances taking part in that process.

E. C. B.

Formation of Glycogen in the Liver. By v. MERRING (*Pflüger's Archiv. f. Physiologie*, xiv, 274—284).—The point at issue is whether (as held by Pavy, Dock, and others) glycogen is formed by direct transformation from bodies introduced into the system, or whether (according to Tieffenbach and Weiss) these bodies only contribute indirectly to the accumulation of glycogen in the liver by being oxidised, and thus to a certain extent protecting and sparing the glycogen. To elucidate this point, the author experimented by introducing numerous substances into the system of rabbits and dogs, whose livers were rendered as far as possible free from glycogen by previous starvation. The bodies used comprised examples from the groups of carbohydrates, glucosides, alcohols, albuminous bodies, and fats. The rabbits had previously fasted five days and the dogs 18 to 21 days.

The author's results show that the assimilation of the following substances produces a considerable accumulation of glycogen in the liver, viz., grape-sugar, cane-sugar, milk-sugar, fruit-sugar, inulin, lichenin, glycerin, arbutin, gelatin, and albuminates (egg-albumin, fibrin, casein). After the introduction, on the other hand, of inosite, mannite, quercite, erythrite, and fats, no appreciable quantities of glycogen are found. A closer chemical examination showed that the glycogen obtained after feeding with carbohydrates, meat, and albuminates was in all cases the same. In conclusion, the author examined the livers of four diabetic patients. In two of them, who died suddenly, both glycogen and sugar were found in the liver in large quantities, and the glycogen did not differ in any way from that ordinarily found in the liver. In the other two cases, in which the excretion of sugar in the urine ceased some hours before death, neither glycogen nor sugar was found in the liver.

E. C. B.

Composition of Horn and Gray-fish Shells. By H. WEISKE (*Land. Versuchs-stat.*, xx, 35—49).—If a piece of stag's horn be placed in water at the ordinary temperature, it imparts to the latter after some time an intense red colour. The horn of the roebuck, however, does not produce this coloration. On evaporating the liquid to dryness, the colour changes to brown, and the dried residue, after treatment with common salt and acetic acid, shows under the microscope numerous crystals of hæmin. The composition of this dried extract is as follows:—

Organic matter	79.90
Ash	20.10

The ash consists of—

100.00

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	CO ₂ .	SO ₃ .	Cl
5.80	16.24	27.77	2.18	2.25	7.78	27.40	3.37	8.33 = 101.12.

In order to determine the amount of extractable matter, the powdered horn was digested first in ether and afterwards in water, and the extracts filtered, evaporated to dryness, and weighed. The following results were thus obtained :—

	Stag's horn.	Roebuck's horn.
Extracted by ether	0.26 per cent.	0.19 per cent.
„ water	5.76 „	4.55 „

The residue left, after extracting with ether and water, consisted of—

	Stag's horn.	Roebuck's horn.
Organic matter.....	36.32 per cent.	36.78 per cent.
Ash.....	63.68 „	63.22 „

The ash (allowing for carbonic acid expelled by burning) showed the following composition :—

	Stag's horn.	Roebuck's horn.
Lime	51.52 per cent.	51.51 per cent.
Magnesia	1.32 „	1.28 „
Phosphoric acid	39.31 „	39.08 „
Carbonic acid	4.60 „	4.88 „

The spongy part of the stag's horn amounts to about 24.94 per cent. of the total. An analysis of each part gave the following results :—

	Spongy part.	Hard part.
Extracted by ether	0.37 per cent.	0.11 per cent.
„ water	6.88 „	3.51 „

The residue left, after extracting with ether and water, consisted of—

	Spongy part.	Hard part.
Organic matter.....	49.89 per cent.	42.31 per cent.
Ash	50.11 „	57.69 „

The ash contained—

Lime	51.53 „	51.58 „
Magnesia	1.32 „	1.33 „
Phosphoric acid	39.43 „	39.79 „
Carbonic acid	4.25 „	4.03 „

For this examination a piece was cut from the middle of a large horn, whereas for the former analyses a complete antler was taken in each case, which may account for the difference in the percentage of ash. The proportion of ash to organic matter varies within certain limits, but the ash itself always shows very nearly the same composition.

In connection with the foregoing researches, an examination was made of the shelly armour of the cray-fish (*Astacus fluviatilis*). The principal constituents of the shell are calcic carbonate and chitin. It also contains a little phosphoric acid and a trace of magnesia.

H. H. B. S.

Some Volatile Products of the Putrefaction of Brain-matter. By F. SELMI (*Gazzetta chimica italiana*, vi, 468—471).—Brugnatelli and also Lefort have asserted that neither phosphoretted hydrogen nor any volatile phosphorus compound occurs amongst the products of animal putrefaction. The author, however, finds that when putrefied brain-matter is distilled in a current of carbonic anhydride, and the distillate collected in a receiver containing an alcoholic solution of nitrate of silver, the latter, on being evaporated to dryness to destroy organic matter, redissolved in water, and tested by the molybdenum reagent, gives abundant evidence of the presence of phosphoric acid. This, however, is not the case when either the urine, the viscera, or muscle in a state of putrefaction are similarly treated. From his experiments he also concludes that putrefied brain-matter does not contain any of the lower acids of phosphorus, but a phosphorised compound of unknown nature. On distilling putrefied brain-matter, large quantities of trimethylamine are given off, and also a substance which produces a red coloration when evaporated with nitric acid.

From these results it is evident that in a toxicological examination for phosphorus it is necessary to keep the brain apart, and to pay no attention to the alliaceous odour evolved by the putrefying matter if the volatile products of the distillation with alcohol yield no phosphorus when agitated with carbon bisulphide.

The author concludes with some remarks on the physiological relations of these phenomena, comparing them with those which take place in the green portions of plants. C. E. G.

On the Form of Combination of Urea in the Liver, &c. By IRA-MUNK (*Chem. Centr.*, 1876, 230).—The author has determined the relative amounts of urea in the blood and the liver of the same animal. The urea was precipitated from the extract of the blood or liver with Liebig's solution; the precipitate was then decomposed with sulphuretted hydrogen, and the urea determined in the filtrate by Bunsen's method of heating with barium chloride and ammonia. The liver was bruised with alcohol, and then treated in the same manner as the blood.

The following results were obtained:—

Dog.	1.	2.	3.	4.
Blood .	0.053 p.c.	0.052	0.024	0.041
Liver .	0.039	0.046	0.020	0.030

In the fourth experiment the extractive matter was removed by precipitation with lead acetate. In every case there was less urea in the liver than in the blood, so there is no reason to suppose that urea is formed in the liver. Proof is, however, required that the ammoniacal barium chloride did not decompose other substances besides urea. Only creatinine comes here into consideration, but it is contained in blood only in very small quantity, and may therefore be neglected. If, however, urea is to be determined in urine secretions, the creatinine should be precipitated with zinc chloride, and the filtrate used for the determination of urea.

W. R.

A Levorotatory Substance in Normal Urine. By H. HAUS (*Chem. Centr.*, 1876, 311).—The author has found that all healthy urine causes the plane of polarised light to rotate in a tube one decimeter in length $-3'$ to $-10'$ to the left. This property is less strong in urine passed during the night than in that passed in the day time. It is not affected by the presence of acids or alkalis, except strong sodium or ammonium carbonate, or by evaporation to small bulk; but if the urine is not too much concentrated, the intensity of the reaction increases inversely to the bulk of the liquid.

Alcohol dissolves the substance from the syrupy urine; and animal charcoal, employed for the purpose of decolorising the liquid, reduces the rotating power; but the substance may be washed out of the charcoal with distilled water. The active substance is not precipitated by basic lead acetate, which may therefore be used to decolorise the liquid. When the excess of lead is removed with ammonia or sulphuric acid, the substance is also precipitated, and remains in the lead sulphide when sulphuretted hydrogen is passed through the liquid. But boiling water, or, better, alcohol, dissolves a substance out of the lead sulphide which deflects to the right. The solution does not reduce copper oxide, and gives a brown-yellow colour with sodium hydroxide and with nitric acid. W. R.

Double Decomposition of Potassium Bromide and Sodium Chloride in the Animal Organism. By J. H. BILL (*Amer. Journ. of Sci.* [3], xii).—Some time ago the author, in conducting a physiological research on the action of the bromides, observed the facts now communicated by him with regard to the demonstration of the proposition that potassium bromide and sodium chloride brought together in solution undergo double decomposition. If 5—6 grains of potassium bromide are given to a healthy man, the urine of the succeeding 24 hours will show the following changes. Nearly all the potassium ingested as bromide will be found united with chlorine, augmented according to the amount of bromide taken, the sodium scarcely altered in quantity, the sulphates and phosphates unchanged. Only a very little bromine will be found. Bromides, however, may be detected for two weeks after the last dose taken; excess of potassium will be found only after the first day. The author can account for these facts only on the supposition that the potassium bromide ingested was decomposed by the sodium chloride of the blood, potassium chloride excreted by the urine, and sodium bromide retained in the blood as a substitute for the sodium chloride. He gives the following average results of three analyses when no bromine was taken, and of six analyses whilst the body was under the influence of 5—10 grains of bromide. The results show the amounts of the whole 24 hours. The method of analysis was to incinerate the urine, and from the ash to separate alkaline earths, sulphates, and phosphates. The sodium and potassium were then estimated as chlorides.

	Potassium. grains.	Sodium. grains.	Chlorine. grains.	Bromine. grains.
No bromide taken . . .	4.21	7.67	9.56	—
Seven grains (average) of bromide taken .. }	6.52	7.82	11.45	0.04 .

J. M. T.

Influence of Salicylic Acid and Sodium Salicylate on Bodily Temperature. By M. GEDL (*Chem. Centr.*, 1876, 509).—Doses of 5 and 3 grams of the acid and of its sodium salt were administered. A very slight decrease of temperature was noticed in some cases: generally the daily fluctuations of temperature noticeable under normal conditions were rendered less apparent. M. M. P. M.

Chemistry of Vegetable Physiology and Agriculture.

The Function of Chlorophyll in the Vine (*Vitis vinifera*). By G. BRIOSI (*Gazzetta chimica italiana*, vi, 457—460).—After noticing the labours of various physiologists in one of the greatest modern discoveries in vegetable physiology, the formation of starch in the chlorophyll granules from carbonic acid under the influence of light, the author says that he has frequently had occasion to observe that starch is never found in the chlorophyll grains in the leaf of the vine; fatty matters and glucose also are present only in insignificant quantities, whilst tannin is abundant, being found, not only in the epidermal cells, but also in those containing chlorophyll, and most largely in the upper layers of the leaf exposed to the direct action of the light, where the action of the chlorophyll is most energetic.

The author does not, however, consider this fact, even when taken in conjunction with other unpublished observations, sufficient to warrant the conclusion that the tannin is formed in the chlorophyll in the vine leaves, as the researches hitherto made on the function of tannin indicate that it is a secondary product, or product of degradation.

It is generally admitted, at the present time, that the liber serves for the transport of the proteid substances, whilst the carbohydrates and fatty matters circulate by means of the parenchyma; but the author has shown (*Botanische Zeitung*, 1873, No. 20), that starch granules are scarcely ever wanting in the first-named tissue. It is of interest, also, to know that in the liber of the vine, besides starch, tannin is invariably present, which may, perhaps, assist in determining the physiological action exercised by that substance in the vine. C. E. G.

Change of Composition in Potatoes during Disease. By J. H. JELLETT (*Proceedings Roy. Irish Academy* [2], ii, 736).—From the same variety of potato four samples were taken—I. Perfectly sound potato. II. Sound part of potato in which disease had just

commenced. III. Sound part of potato in which disease was far advanced. IV. Discolored part of diseased potato. The water, sugars, and nitrogen found, were as under:—

	Per cent. of fresh tuber.				Per cent. of dry tuber.			
	I.	II.	III.	IV.	I.	II.	III.	IV.
Water	73·09	77·24	80·04	79·28				
Sucrose	·08	·29	1·14	·21	·29	1·27	5·71	1·00
Glucose	·42	·65	·76	·40	1·59	2·85	3·81	1·93
Nitrogen	·27	·35	·31	·25	1·00	1·53	1·55	1·26

The percentage of nitrogen appears to increase considerably before the visible commencement of disease; at the same time the sugar largely increases, and reaches its maximum somewhat later than the nitrogen. When actual discoloration appears, a great loss of sugar, and a smaller one of nitrogen, takes place.

R. W.

Phosphatic Guanos.—By A. VOELCKER (*Journ. Roy. Agri. Soc.* [2], xii, 440—459).—In Angamos guano, from the Bolivian coast, we have the best example of the rapidly-dried recent excrement of sea-birds; this guano is acid to litmus, and contains 19—21 p.c. of nitrogen. Exposed to the weather in various climates, bird-dung undergoes change, and guanos of various qualities are produced. The ultimate effect of rain is to destroy the organic matter; the guano remaining is then said to be “phosphatic,” and contains very little nitrogen. These phosphatic guanos are of great value as materials for high-class superphosphate. The annexed table gives more or less complete analyses of a number of phosphatic guanos. In many instances, the bases present are insufficient to form tribasic salts with the phosphoric acid; this is especially the case in the stony masses, known as “crust” guanos, frequently found in deposits much altered by weather. Mejillones guano is a deposit near the Coast of Bolivia, estimated at several million tons; the phosphoric acid, on an average of 12 analyses, is equal to 72·1 p.c. tricalcic phosphate. Some of the guanos from islands in the Gulf of California contain over 80 p.c. of tricalcic phosphate. Curaçoa Island is on the coast of Venezuela; a rock-phosphate from Great Curaçoa yielded 81·9 p.c. tricalcic phosphate. The five guanos next mentioned in the table are of little importance. Baker, Howland, and Jarvis Islands lie near the equator, in the Pacific Ocean, their guano is now nearly exhausted; the analysis of Jarvis Island guano represents the present inferior importations; sulphate of calcium is often present. Shaw’s, Malden, Enderbury, and Starbuck Islands are coral islands in the South Pacific Ocean, the guano is of high quality, but apt to be contaminated with fragments of the coral rock. The South American guanos are seen, by the analyses, to contain a large quantity of water and sand, and to be richer in nitrogen than the others mentioned; they vary much in composition. Patos Island is on the coast of Lower California. Bird’s Island belongs to the Pacific group.

PERCENTAGE COMPOSITION OF PHOSPHATIC GUANOS.

	Guil of California.		Curacao Island	Quito Serrano Island.	Petrel Island.	Coral Island.	Booby Island.	McKeen Island.	Baker Island.	Howland Island.	Jarvis Island.	Shaw's Island.	Flint Island.	Malden Island.	Enderbury Island.		Starbuck Island.	
	2.	1.	9.	1.	1.	1.	1.	1.	1.	2.	1.	1.	1.	9.	Powder.	Crust.	Powder.	Crust.
Number of Analyses.																		
Water.....	7.68	4.83	11.07	8.50	9.51	7.04	6.10	12.55	12.05	11.42	11.27	13.67	13.26	5.76	8.76	8.33	11.56	8.75
Loss on ignition.....	6.33	12.72	7.11	33.46	30.50	11.76	10.18	9.59	6.25	6.38	9.93	34.69	37.13	5.67	8.81	6.45	7.25	45.57
Phosphoric acid*.....	33.46	34.33	31.64	32.44	30.50	35.29	21.47	22.68	32.32	34.12	23.88	43.26	43.43	33.85	28.74	37.79	33.61	45.57
Lime.....	37.01	37.36	40.41	39.41	36.44	41.76	45.36	36.24	42.34	41.86	37.18	43.26	43.43	45.43	40.76	41.96	41.04	40.94
Magnesia.....	3.13	1.76	—	—	—	—	—	—	.41	—	—	—	—	—	—	—	1.16	.64
Alkali salts.....	5.69	5.54	—	—	—	—	—	—	1.78	—	—	—	—	—	—	—	3.43	.47
Sulphuric acid.....	3.23	—	—	—	—	—	—	—	1.19	—	—	—	—	—	—	—	.88	—
Carbonic acid.....	.91	.46	2.64	—	—	—	—	—	2.99	—	5.02	—	—	3.95	7.26	1.46	1.05	—
Siliceous matter.....	1.86	1.69	.21	2.55	5.50	.60	.09	.79	.14	.22	.09	.85	.19	.10	.09	.06	.02	.07
Nitrogen.....	.89	1.04	—	—	—	.38	—	.26	[.53]	—	—	—	—	—	.38	—	.39	—
*Equal to tricalcic phosphate ...	73.04	74.94	69.01	70.82	66.56	77.05	47.62	49.56	70.55	74.46	52.13	75.73	81.05	73.89	62.74	82.49	73.67	99.48

Number of Analyses.	Falkland Islands.		Patagonian.		Patos Island.	Bird's Island.
	1.	1.	1.	1.	1.	1.
Water.....	33.43	35.96	21.46	6.59	14.35	6.92
Loss on ignition.....	21.42	26.07	11.74	10.23	10.24	4.80
Phosphate of calcium.....	32.04	22.01	27.61	23.44	53.48	80.41
Carbonate of calcium.....	2.52	5.64	2.99	—	2.93	6.38
Sulphate of calcium.....	—	—	—	—	—	—
Alkali salts, &c.	6.22	7.34	6.07	9.05	4.63	1.34
Siliceous matter.....	4.37	3.08	30.18	50.69	14.72	.12
Nitrogen	4.31	4.42	1.83	.90	.96	—

R. W.

The Plant-nourishing Value of Calcium Salts.—By J. BOEHM (*Chem. Centr.*, 1876, 250—256 and 265—267).—It is first proved experimentally that mineral matter is absolutely required by the growing plant in order that it may avail itself of the excess of nourishment stored in the seeds: and that the amount of mineral matter contained in the seeds is of itself insufficient to enable the plant to make use of the whole of the nourishment present in these seeds. The experiments were carried out on scarlet runners.

It is then shown that without lime salts the growing plants soon wither away and die.

Finally, that the lime salts do not participate directly nor indirectly in the formation of starch. M. M. P. M.

Influence of Soil on the Nitrification of Nitrogenous Organic Substances in Manures. By BOUSSINGAULT (*Chem. Centr.*, 1876, 343).—It has been frequently noticed that nitrification takes place, in presence of oxygen and water, of the nitrogen contained in soil, and that the total amount of nitrogen does not increase, showing that no nitrates are formed from the nitrogen of the air. From experiments lasting over five years, in which pure sand, washed and ignited, washed and dried chalk, a sandy soil containing 0.02 of lime, and the same soil without lime were respectively mixed with nitrogenous organic substances, such as straw, meal, bone-earth, horn-filings, wool-refuse, horse-flesh, and horse-blood, it was found by numerous analyses that in the sand as well as in the chalk, very little nitrogen had been converted into nitrates; this shows that the presence of lime has little influence in promoting nitrification. On the other hand, ordinary arable soil manifested great influence, about half the nitrogen present having been converted by its influence into nitrates. 100 grams of blood gave 0.39 gram of nitric acid, derived solely from the blood, and equivalent to 0.1 gram of nitrogen. W. R.

Analytical Chemistry.

Determination of Nitric Acid by Indigo. By R. WARINGTON (*Chem. News*, xxxv, 45—47, 57—59).—The author first describes the method employed by Boussingault, in which the nitrate is boiled with hydrochloric acid, and solution of indigo added till a sap-green colour is permanently obtained. Boussingault destroys organic matter, when present, by a preliminary distillation with peroxide of manganese and sulphuric acid. The experiments made by the author with the method introduced by Marx, and since improved by Trommsdorff, Goppelsröder, Bemmelen, and Sutton, are next detailed. In this method the reaction is brought about by mixture with oil of vitriol, without the use of artificial heat. The indigo employed was a solution of "indigo-carmin" (sulphindigotate of sodium); the solution of pure nitre contained 0.01011 gram in 10 c.c.; the oil of vitriol was distilled acid.

The author found—I. That the maximum amount of indigo is consumed only when a sufficiency of indigo is present with the nitrate before the addition of oil of vitriol. The plan adopted by Marx of mixing the nitrate solution with twice its volume of oil of vitriol, and then immediately running in the indigo, always consumes less indigo than the nitrate is capable of oxidising. The full amount of indigo can only be ascertained by a series of approximating experiments, in which the oil of vitriol is suddenly added to the previously mixed nitrate and indigo. II. The amount of indigo required depends greatly on the proportion of sulphuric acid present, and within certain wide limits the amount of indigo is less as the proportion of sulphuric acid is greater. With 10 c.c. of nitre solution 11.3 c.c. of indigo were required, when the indigo and nitre were mixed with their own volume of oil of vitriol; but 8.9 c.c. of indigo were sufficient when two volumes of oil of vitriol were employed. III. The full amount of indigo is consumed only when the temperature of the mixture remains sufficiently high during the reaction; 100°, 110°, and 120°, are given by various writers as the minimum temperature. When the reaction was immediate, artificial heat was found unnecessary; but when, through dilution of the nitrate, small volume of the liquid, weakness of the vitriol, &c., the reaction was tardy, the temperature of the flask containing the mixture must be maintained by a paraffin or chloride of calcium bath, or the results will be too low. IV. The true tint of final reaction is a dull brown, which precedes the commencement of green; the brown tint becomes green when suddenly diluted with water. If a solution of sublimed indigotine in sulphuric acid is employed, the tint passes at once from gold to green without an intermediate brown stage. V. When a nitrate solution is diluted, it apparently requires distinctly less indigo per unit of nitrate if a double volume of oil of vitriol be employed; but if a single volume is used, the difference is very slight, and in the contrary direction. If two volumes of sulphuric acid are employed, the indigo must, therefore, be standardised with nitre solutions of several dilutions to ascertain the value of different parts of the scale. VI. The influence of chlorides is slightly to diminish the indigo required. With .08 to .10 gram of chloride of sodium in 10 c.c. of nitre solution, the reducing effect of 100 chloride of sodium was equal to 1.16 nitre. With much chloride the final tint is a bright green. VII. Some kinds of organic matter have a powerful reducing action. Cane-sugar had a greater effect the larger the proportion of sulphuric acid and the more dilute the nitrate; with a $\frac{1}{16}$ th nitre solution, and a double volume of oil of vitriol, 100 of sugar had a reducing effect equal to 62.3 nitre. The soluble humic matter of soils was apparently without influence, determinations of nitrate in a kitchen garden soil by the mercury method, and by the indigo method, giving accordant results: only one volume of sulphuric acid was used in this experiment.

R. W.

The Quantitative Determination of Boric Acid by Baryta.
By PAUL BERG (*Zeitschr. Anal. Chem.*, xvi, 25—33).—Boric acid is completely precipitated from its aqueous solution by addition of baryta-

water in such quantity, that to every molecule of B_2O_3 from $1\frac{1}{2}$ to 2 molecules of BaO are added, and provided alcohol is added until the liquid contains 55—60 per cent. of alcohol. After standing 24 hours, the precipitate, consisting of $BaO.B_2O_3 + 4Aq$, settles in a crystalline condition, and may be washed with 75 per cent. alcohol, dried over oil of vitriol, and weighed.

The operations must be carried out in an apparatus which prevents precipitation of barium carbonate by atmospheric carbon dioxide.

Boric acid must be separated from sodium borate by addition of hydrobromic acid to strongly acid reaction before applying the above method of estimation, the sodium and barium bromides formed being readily soluble in alcohol. Other metallic borates must be converted into sodium borate by boiling with sodium carbonate solution, or by fusion with solid sodium carbonate. If a larger proportion of baryta-water is used in the precipitation, crystals of barium hydrate are separated on addition of alcohol; they can be removed from the precipitate by washing with weak alcohol. Alcohol of 60 per cent. dissolves only $\frac{1}{1000}$ of its weight of the barium borate precipitate. Analytical results which accompany the paper prove that the method is accurate, and that with proper precautions for avoiding exposure to the air, no barium carbonate is present in the precipitate. F. C.

Volumetric Estimation of Sulphuric Acid by Barium Chloride Solution in Acid Liquids. By G. BRÜGELMANN (*Zeitschr. Anal. Chem.*, xvi, 19—22).—The author describes a modification of Wildenstein's arrangement (*Zeitschr.*, i, 431—437), for rapidly filtering off a portion of the liquid under titration in order to determine the point of complete precipitation. The liquid to be titrated is contained in a beaker, and is heated over a gas flame to the temperature most favourable to the rapid precipitation of barium sulphate. The apparatus for removing filtered samples of liquid from the beaker consists of a small funnel, containing filter-paper and cotton wool, and hanging in the liquid; this is joined to a longer tube outside, so as to form a syphon, by means of a piece of india-rubber tubing, which forms the bend of the syphon. This syphon-filter is filled with hot water, its longer limb closed by a piece of india-rubber tubing and pinch-clamp, and the funnel suspended in the liquid in the beaker. The arrangement proved very useful, and yielded very accurate results in determinations of sulphur in animal and vegetable substances, and in coal gas. F. C.

On the Purification of the Barium Sulphate Precipitates obtained in Quantitative Analyses. By G. BRÜGELMANN (*Zeitschr. Anal. Chem.*, xvi, 22—24).—The method recommended by Fresenius for the separation of salts carried down from solution and retained by a barium sulphate precipitate is modified as follows. Several drops of rather strong hydrochloric acid are poured upon the ignited precipitate in the crucible, and a few c.c. of water added; the lumps are then broken up with a small glass rod, and the liquid warmed short of boiling for about two minutes, then poured off through a small filter. This process is repeated until on washing the precipitate with water

the filtrate, on being tested by a few drops of sulphuric acid, is found free from barium; from five to eight repetitions were usually sufficient. If larger quantities of hydrochloric acid are employed, or the liquid is heated to boiling with the precipitate, decomposition of the barium sulphate may occur. The volumetric process of estimation is always less troublesome, unless only a few estimations are to be made, and the standard solutions are not at disposal.

F. C.

Estimation of Phosphorus and Arsenic by Ammonium Molybdate. By CHAMPION and PELLET (*Bull. Soc. Chim.* [2], xxvii, 6).—The authors consider that it is better to weigh the phosphomolybdate, than to convert it into ammonio-magnesium phosphate and determine the phosphoric acid from this. As the concentration of the solutions exercises a great influence on the time required for precipitation, certain precautions are necessary to ensure a rapid mode of working: 100 grams of molybdic acid are dissolved in ammonia (150 c.c. ammonia and 80 of water) and the solution added drop by drop to 500 c.c. of pure nitric acid (sp. gr. not given), and 300 of water. A quantity of the molybdate representing about 50 times the weight of the phosphoric acid in molybdic acid is placed in a basin; it is rendered alkaline by ammonia; and the solution containing the phosphoric acid, after being concentrated as much as possible, is added; the mixture heated to 70–80°, and nitric acid added until a yellow colour is produced. Collect, wash, and dry the precipitate at 100–110°. Arsenic acid may be determined in the same way.

C. E. G.

Determination of Alkaline Sulphates. By F. JEAN (*Compt. rend.*, lxxxiii, 973–979).—To the aqueous solution of the substance a slight excess of baryta-water is added, and then Seltzer water, which precipitates the excess of baryta. The liquid is separated by decantation, boiled, and filtered with the first precipitate. The precipitate having been washed, the filtrate is coloured with litmus and neutralised with a standard solution of sulphuric acid. The amount of acid necessary is of course exactly equal to that which was originally combined with the alkalis.

This method is of great advantage where sulphates of lime, magnesia, &c., are present.

F. D. B.

Estimation of Phosphorus in the Form of Ammonio-phosphomolybdic Salt. By SERGIUS KERN (*Chem. News*, xxxv, 1).—The following method for the analyses of irons and steels, being a modification of that of Eggertz, is recommended:—

1 gram of the specimen is dissolved in 20 c.c. of aqua regia, and the phosphorus is precipitated by Eggertz's method; the resulting yellow precipitate, separated from the solution, is dissolved on the filter in ammonia, and in the filtrate obtained; is slightly acidulated by hydrochloric acid; the phosphorus is precipitated in the form of phosphoammonio magnesium salt $[\text{Mg}(\text{NH}_4)\text{PO}_4]$ by "magnesium mixture," prepared by dissolving 1 gram of MgSO_4 and 1 gram of NH_4Cl in 8 c.c. of water mixed with 4 c.c. of ammonia. The precipitation is finished in 15 to 20 hours; the precipitate is filtered from the solution, washed

with water containing half a per cent. of ammonia, and first gently heated in a platinum crucible till free ammonia and water are evaporated; the crucible is next ignited for 30 to 40 minutes, and the received $\text{Mg}_2\text{P}_2\text{O}_7$ is weighed. This salt contains 13.51 per cent. of phosphorus.

E. W. P.

Volumetric Estimation of Arsenic. By P. CHAMPION and H. PELLET (*Bull. Soc. Chim.* [2], xxvi, 541—544).—The authors here give the details of a process devised by them for the volumetric estimation of arsenic, and based on the following principles:—1st. Transformation of the arsenic into sulphide. 2nd. Solution of the sulphide in ammonia, and saturation with acetic acid. 3rd. Estimation of the arsenic by iodine, in presence of starch. The method is applicable to any quantities of arsenic, and is sufficiently delicate to be employed in poisoning cases.

R. R.

A new Method for the Gravimetric or Volumetric Determination of Phosphorus, Arsenic, Sulphur, Chlorine, Bromine, and Iodine in Organic Substances, and in Vegetable and Animal Compounds, as well as for the Determination of Sulphur in Coal Gas. By G. BRÜGELMANN (*Zeitschr. Anal. Chem.*, xvi, 1—21).—The author brings forward two modifications in the methods already described by him in the *Zeitschr.*, xv, 1—27, 175—186; *Chem. Soc. J.*, 1876, i, 743, by which the processes there employed for determining phosphorus, sulphur, and chlorine in organic substances become applicable to arsenic, bromine, and iodine. Substances which are explosive when burnt in oxygen also become manageable by the new method.

The advantages claimed are:—

1st. That each of the above six elements can be gravimetrically determined in from three to four hours.

2nd. That even when a large weight of substance is employed, only small quantities of reagents are necessary, and the contents of the tube are thus soluble in a small quantity of liquid.

3rd. That each of the six elements can be determined in separate parts of the same solution, and that the combustion of two different substances may be carried out in the same tube.

1. *First Modification.*—This is applicable to substances which, when heated in a current of oxygen, evolve easily inflammable vapours; such are almost all non-volatile organic solids and liquids. In these cases a current of air is used at first, and the combustion is completed in a stream of oxygen. A layer of asbestos of at least 15 centimeters is requisite.

Cacodylic acid and carbothialdine treated by this method underwent quiet and regular combustion. Only in the case of phosphorus compounds, where the substance is mixed with excess of soda-lime, may the asbestos be dispensed with, and combustion made at once in oxygen.

Liquids which are readily or not very difficultly volatile, should be burnt at once in oxygen, else the excess of oxygen requisite for their combustion is not obtained. In the case of compounds containing

arsenic, the soda-lime should be separated from the asbestos by pieces of glass, or by an asbestos plug, instead of by platinum, as platinum is considerably attacked in presence of arsenic. Arsenic-compounds, after having been sublimed in the air-stream into the asbestos, must be burnt in a carefully maintained excess of oxygen, as metallic arsenic is liable to be separated on the soda-lime by the action of carbon. The arsenic is thus obtained in the form of arsenate, which is well suited for estimation as uranium arsenate, either by a modification of Bødeker's volumetric method described below, or gravimetrically by Werther's method (*Fres. Quant. Anal.*), the contents of the tube being dissolved in water and hydrochloric or nitric acid. The soda-lime (or lime) must be free from iron and alumina.

Second Modification.—This consists in substituting soda-lime for granulated lime, it renders the process applicable to the estimation of bromine and iodine. A soda-lime which possessed the maximum power of arresting bromine and iodine, together with a minimum corrosive action on the glass, was made by dissolving 20 grams of sodium hydrate in 60 of water, pouring this hot solution upon 80 of powdered marble lime in a large porcelain crucible, stirring at once quickly, so as to mix the solution thoroughly with the lime before the latter slakes and becomes too stiff to be easily stirred; the water is then driven away by ignition, and the mass granulated.

After combustion, the contents of the tube are heated with water until disintegrated, and the cooled liquid gradually mixed with excess of dilute nitric acid. This solution can be at once precipitated, or titrated with silver nitrate solution in the case of chlorine or bromine; but before determining iodine, the free iodine and sodium iodate must be converted into hydriodic acid by addition of sulphurous acid. Volhard's volumetric method, by use of silver nitrate and ammonium sulphocyanide (this *Zeitsch.* xiii, 171—175), is very convenient for the estimation of bromine, chlorine, and iodine. A modification of Wildenstein's method for volumetric estimation of sulphuric acid is described below, it has given good results; it is preferable to the gravimetric method on account of the extreme difficulty of obtaining a pure barium sulphate precipitate for weighing.

The new method is inapplicable to determining phosphorus or arsenic in presence of much iron or aluminium, but the minute quantities of these metals often present in organic substances do not affect the results by the volumetric method.

The six elements under consideration may be determined either successively in one portion, or in different portions of the same solution, and since any one organic substance rarely contains more than one of the above elements, weighed quantities of two different substances containing different elements may be burnt in the same tube and at the same time, and using the same lime or soda-lime: three different substances can hardly be simultaneously burnt with advantage, since this involves using too small a weight of each, or too long a layer of lime. The weight of substance used varies from 2 to 6 decigrams. Soda-lime is on the whole preferable to lime. Only in the case of phosphorus, arsenic, or sulphur is hydrochloric acid applicable for the solution of the contents of the tube. If an excess of oxygen

is maintained during the combustion of organic compounds, and a sufficiency in that of organic tissue, &c., and the process is not too rapidly carried on, the layer of lime or soda-lime 10 centimeters in length amply suffices for the absorption, the last 2 centimeters usually remaining pure. Substances must be prevented from burning with a flame by proper regulation of the stream of air or oxygen. Tables of results obtained by the above methods conclude the paper.

F. C.

Volumetric Estimation of Arsenic Acid and Phosphoric Acid by Uranium Solution. By G. BRÜGELMANN (*Zeitschr. Anal. Chem.*, xvi, 22—24).—Bödeker's method (*Ann. Chem. Pharm.*, cxvii, 195, and *Fres. Quant. Anal.*) is modified in such a way as to make it more simple and trustworthy.

After the arsenate has been dissolved in water, nitric acid, or hydrochloric acid, sodium hydrate or ammonia is added gradually to decidedly alkaline reaction, then acetic acid is added until the liquid is strongly acid; the operations are carried on with the cold liquid to hinder any separation of phosphates or arsenates of barium, strontium, or calcium. The addition of sodium or ammonium acetate is unnecessary, and since very little of this salt is present, potassium ferrocyanide can be used as an indicator unless the liquid is very dilute, and the value of the uranium solution is at once given by its strength, no correction being necessary.

The uranium solution should contain about 20 grams of uranium oxide to the litre, and must be free from mineral acids. The liquid to be estimated must not exceed 50 c.c., this volume being secured by division or evaporation. The solution is first mixed in the cold with almost the requisite quantity of the uranium solution, and then after each addition it is boiled for several minutes, until after two successive periods of boiling a few drops give a brownish tint to a drop of feebly coloured potassium ferrocyanide solution. The estimations were free from the loss always experienced by Fresenius when large quantities of calcium were in solution; this error was probably avoided by securing the absence of large quantities of sodium acetate, and by preventing the separation of calcium phosphate on boiling, by only boiling the solution after almost the requisite quantity of uranium solution had been added. To secure the latter result when unknown quantities of phosphoric acid were present, a preliminary titration was made, which gave the volume of uranium solution to within 1 c.c., and in the subsequent determination the quantity was carefully determined to 10.1 c.c. (corresponding to 0.00022 P and 0.00053 As). F. C.

On the Estimation of Sulphur in Coal Gas. By G. BRÜGELMANN (*Zeitschr. Anal. Chem.*, xvi, 24).—The author examined the gas supply of Leipzig by his method (*Zeitschr.*, xv, 175) for sulphur, and on the 12th and 15th of July found none. He considers that this result is not due to the volume of gas used by him (10 litres) being insufficient, since his method determines 0.0029 gram of sulphur in 10,000 c.c. of gas, when only 2,883 c.c. are burnt, and gas in England

is considered pure if it contains a maximum quantity of 0.0057 gram per 10,000 c.c. F. C.

A Delicate Spectroscopical Reaction for Alumina and Magnesia. By HERMANN W. VOGEL (*Deut. Chem. Ges. Ber.*, ix, 1641—1646).—A dilute aqueous solution of pure purpurin shows a weak absorption in the yellow, and a stronger in the green, between F and b. This absorption becomes more intense when ammonia is added, and disappears on adding dilute acetic acid, a faint absorption in the blue alone remaining. But when to a very dilute aqueous solution of purpurin a dilute solution of alum is added, the liquid becomes red, and gives two strong absorption bands between D and E and b and F. This reaction, which is also produced by other aluminium salts, is best seen in a very weak alkaline solution; it is weakened but not destroyed by acetic acid.

Magnesium salts give the same bands, only that in the yellow is stronger than the other, but the least excess of acetic acid destroys the spectrum. The least traces of magnesium and aluminium can be detected by this reaction, which is not shown by the salts of iron, manganese, zinc, the alkali-metals or those of the alkaline earths; but it does not appear when salts of iron or zinc are present in excess.

The author then describes the methods for separating these salts and the pocket-spectroscope which he uses, and gives drawings of this apparatus and the curves of the different spectra. C. S.

Calculation of the Percentage of Chemically Combined Carbon in Analyses of Steels by Eggertz's Colorimetric Method. By SERGIUS KERN (*Chem. News*, xxxv, 1).—Owing to the want of published tables for calculating the amount of carbon present in steel, it is proposed to proceed as follows:—A solution of normal steel (0.1 gram dissolved in 8 c.c. of nitric acid) containing 0.31 per cent. of carbon, is compared with the colour of a like solution of the specimen.

In calculating the percentage of carbon two cases may happen:—

1. The specimen solution is *darker* in colour than the normal solution.
2. The specimen solution is *lighter* in colour than the normal solution.

I. *The specimen solution is darker.* 8 c.c. of the normal solution contain 0.31 per cent. of carbon: hence 1 c.c. of the same solution contains—

$$\frac{0.31}{8} = 0.0038 \text{ per cent. of carbon.}$$

In comparing the specimen solution it was diluted by 1 c.c. of nitric acid, in order to obtain the tint of the normal solution. The total volume of this solution is therefore 9 c.c.

$0.0038 \times 9 = 0.0342$ per cent. of chemically combined carbon in the specimen analysed.

II. *The specimen solution is lighter.* In this case the normal solution must be diluted to obtain an equal tint with the specimen solution. 8 c.c. of the normal solution were diluted by 2 c.c. of nitric acid. The total volume of the liquor is hence 10 c.c. One c.c. of this solution contains—

$$\frac{0.31}{10} = 0.031 \text{ per cent. of carbon.}$$

The volume of the specimen solution remains always in this case 8 c.c., so that the percentage is very easily found out:—

$$0.031 \times 8 = 0.248 \text{ per cent. of carbon in the analysed specimen.}$$

By means of these calculations, knowing the per cent. of carbon in the normal steels, tables may be very easily calculated.

E. W. P.

On the Analysis of Illuminating Gas. By M. BERTHELOT (*Compt. rend.*, lxxxiii, 1255).—Up to the present time chlorine and fuming sulphuric acid have been the only absorbents used in the determination of hydrocarbons; the author has, however, found it advantageous to substitute bromine for chlorine, and boiled sulphuric acid for the Nordhausen acid.

Boiled sulphuric acid (*i.e.*, ordinary sulphuric acid concentrated as much as possible by boiling) does not act on benzene, and acts on ethylene and acetylene so slowly as to permit of their separation from their more highly condensed homologues. It also produces sulphur dioxide with much greater difficulty than Nordhausen acid does.

He has found that chlorine has the disadvantage of decomposing water in presence of hydrocarbons, and forming carbonic acid. Bromine does not act in this way.

When the gas contains only traces of the hydrocarbons removable by boiled sulphuric acid, fuming nitric acid may be used for the determination of benzene. It is used over water by means of peculiar contrivances, and may be applied immediately after the removal of carbon dioxide. If, however, the gas contains much ethylene, acetylene or their homologues, as is the case with the gases obtained from boghead and cannel coal, these must be removed before the application of the nitric acid.

The following is the method recommended by the author for the analysis of gases rich in hydrocarbons:—

1st. *Carbon dioxide* and *hydrogen sulphide* are removed by solid potash; or the sulphide may be removed by cupric sulphate.

2nd. *Oxygen* is removed by pyrogallate.

3rd. *Water* is estimated by dried calcium chloride.

4th. *Carbon disulphide* is estimated by potash moistened with alcohol; and the alcohol vapour is removed by dry calcium chloride.

5th. The gas is then agitated over mercury with about one-twentieth its volume of boiled sulphuric acid for about a minute. This removes homologues of ethylene and acetylene. The gas (transferred to another eudiometer) is freed from any sulphurous acid that may have been formed by means of slightly moist potash.

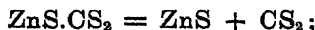
6th. *Ethylene and Acetylene*.—The gas is transferred to a dry flask and agitated with a tenth of its volume of sulphuric acid for three-quarters of an hour.

7. *Benzene and its Homologues*.—The residual gas is transferred over water to a eudiometer, and fuming nitric acid passed into it with the precautions mentioned in the original paper. The benzene is thus entirely absorbed, and its quantity determined.

8th. *Carbonic oxide* is absorbed by acid cuprous chloride. It is as well to perform the operation twice, using each time a volume of the liquid equal to half the volume of gas.

9th. The remaining gas, freed from hydrogen chloride and water, is then analysed by combustion in the usual way, to find the amounts of hydrogen, and of marsh-gas and the other paraffins. C. W. W.

Estimation of Carbon Disulphide in Alkaline Sulphocarbonates. By L. FINOT and A. BERTRAND (*Ann. Chim. Phys.* [5], ix, 142—144).—The authors propose a new method founded upon the instability of zinc sulphocarbonate. Ten grams of the alkaline sulphocarbonate, together with 25—30 c.c. of water and 10 c.c. of a strong solution of zinc sulphate, are introduced into a flask of about 100 c.c. capacity, fitted up after the manner of a carbonic acid apparatus. On mixing the contents of the flask, a yellow precipitate of zinc sulphocarbonate is produced, which decomposes slowly in the cold, but very rapidly at a temperature of 50° or 60°, according to the equation:—



Consequently the loss in weight corresponds with the amount of carbon disulphide contained in 10 grams of the alkaline sulphocarbonate.

The sulphocarbonates of copper and mercury undergo a similar decomposition. H. H. B. S.

Estimation of Sugar by Standard Solutions. By E. PERROT (*Compt. rend.*, lxxxiii, 1044—1045).—A normal solution of copper is prepared by dissolving 39.275 grams of copper sulphate in 1 litre of water. A solution of 25 grams of potassium cyanide in 1 litre of water is also prepared, and of this 10 c.c. are placed in a flask, and about 20 c.c. of ammonia added. The liquid is raised to a temperature of 60° or 70°, and the copper solution is added from a burette, drop by drop, until the blue colour characteristic of copper salts in ammonia appears, when the quantity of copper-solution employed is noted. The analysis of the solution of sugar (which has previously been changed into inverted sugar if necessary) is proceeded with, by adding to it an excess of Fehling's liquid, the reduction being performed over the water-bath. The precipitate is collected, washed, and dissolved in dilute nitric acid, to which a few crystals of potassium chlorate are added. The filtered liquid and washings are made up to a definite bulk, and the quantity of this required to yield the blue coloration with 10 c.c. of the cyanide of potassium solution, to which 20 c.c. of ammonia have been added as before, which indicate the amount of copper precipitated by the sugar. R. R.

Estimation of Tannin. By J. LÖWENTHAL (*Zeitschr. Anal. Chem.*, xvi, 33—48).—The author describes the results of his experience in the estimation of tannin, and considers that his improvements give determinations satisfactory for technical, if not for strictly scientific, purposes. The estimations of tannin from different sources (*e.g.*, sumach and nutgalls) are not comparable, but only those from sumach *inter se*, and from galls *inter se*.

Hammer's method is used, the extract being first titrated after adding indigo-solution so as to ascertain its potassium-permanganate value; the tannin is then precipitated from another portion of the extract, and the permanganate-value of the filtrate ascertained; the permanganate-value of the tannin is obtained by the difference of these results.

For the precipitation of the tannin a solution of glue in water is made and saturated with common salt: it contains 25 grams of glue to the litre. After thoroughly mixing this with the tannin extract, a small quantity of dilute hydrochloric or sulphuric acid is added to assist the separation of the tannin: a vessel with narrow opening should not be used, as the precipitate coagulates into a mass. Of the tannin-extract to be titrated, sufficient is taken to require 0.06 to 0.08 gram of permanganate: 10 grams of sumach are extracted with boiling water, and after cooling, the liquid is made up to 2 litres; to 100 c.c. of this solution 100 c.c. of the glue-solution are added, and to this mixture are further added 50 c.c. of water containing 5 c.c. of HCl (1.12 sp. gr.) or 2 to 2.5 grams of H_2SO_4 . The slight reducing action of the glue-solution upon the permanganate may be safely neglected: the error due to this cause is less when *Hammer's* powdered-skin (*hautpulver*) is employed: this error almost vanishes if $\frac{1}{4}$ of the glue-solution directed to be added is replaced by saturated solution of common salt. The presence of indigo solution is necessary not only as an indicator, but it also prevents the oxidising action of the permanganate extending to any substances in the extract less readily oxidisable than the indigo is itself. The only requisite for making this method quite accurate is the separation of pure tannin and the determination of its permanganate-value: this would ensure the accurate calculation of the quantity of tannin from the difference of permanganate-values. The separation of tannin from its lead-compound by addition of insufficient oxalic acid yielded much purer tannin than the separation by sulphuretted hydrogen.

The sample in which tannin is to be estimated is never dried before being weighed, as it is sold in the undried state. *Oser's* recommendation to add acid during the titration of the indigo solution has been accepted by the author. The determination of glue by precipitation with an excess of tannin, which excess is afterwards titrated, is inexact. Since the quantity of tannin combining with a certain quantity of glue increases with the quantity of tannin present, the author intends to examine the effect of using sodium chloride solution in place of water. Hydrochloric acid is preferred to sulphuric for acidifying. The statements of Wagner that gall-tannin combined with glue putrifies, and that in turkey-red dye-works sumach is never used without galls, are not confirmed by the author's experience.

F. C.

Volumetric Estimation of Phenol. By W. F. KOPPESCHAAR (*Zeitschr. Anal. Chem.*, 1876, 233—245).—The amount of phenol in creasote oil is usually determined by agitating with a known volume of an alkaline hydrate solution, and reading off the volume of hydrocarbons which is gradually deposited. The practical objections to this process are so great that Koppeschaar was led to look for a new process. Landolt has shown excess of bromine water gives a distinct precipitate with very dilute solutions of phenol, owing to the formation of the insoluble tribromophenol, according to the reaction—



This method of estimating phenol is fairly accurate, two test-experiments quoted by Landolt giving 98·6 and 99·1 per cent. instead of the theoretical 100·0. As employed by Landolt, however, this process is in practice open to serious objections, owing to the difficulty in collecting, washing, and drying the very bulky precipitate of tribromophenol. Koppeschaar devised, therefore, a plan for applying the basis of Landolt's process to a system of volumetric analyses. The principle of the new method is as follows:—To a known amount of phenol in aqueous solution a known volume of standardised bromine water is added, in excess of that necessary to convert the phenol into tribromophenol; and the excess of bromine employed is determined in the usual manner by the aid of potassium iodide and sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$.

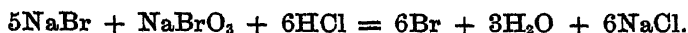
The estimation of the percentage of phenol by this method is made in the following manner. Four solutions are prepared, namely, a solution of starch; a solution of potassium iodide, containing 125 grams per litre; a standard solution of sodium thiosulphate, of such strength that 1 c.c. answers to 1 c.c. of a solution of 5 grams of iodine in a litre of water; and a solution of bromine water, of such strength that 50 c.c., after the addition of 5 c.c. of the potassium iodide solution, require from 18 to 20 c.c. of the standard sodium thiosulphate solution. It is necessary, immediately before employing the bromine water, to estimate its strength in the above manner, and suppose a = the number of c.c. of sodium thiosulphate solution required. Four grams of the creasote containing the phenol are dissolved in water, and the solution made up to the volume of 1 litre. From this solution 25 c.c. are taken and placed in a half-litre flask possessing a closely fitting stopper. The flask is then quickly filled up to the half-litre mark with the standardised bromine water, closed, and well shaken for some time. After standing a quarter of an hour, the contents of the flask are emptied into a beaker containing 10 c.c. of the solution of potassium iodide, and the flask twice rinsed into the beaker. The iodine set free by the excess of bromine is then determined in the usual manner with the standard solution of sodium thiosulphate, with the aid of the starch solution as an indicator. Let b = the number of c.c. of the sodium thiosulphate solution employed. Then the percentage of phenol in the oil examined will be given by the simple equation—

$$\text{Per cent. of phenol} = 0\cdot61753 (9\cdot5 a - b).$$

Koppeschaar quotes numerous test experiments, which show that

the method is fairly accurate, the extreme estimations varying about $1\frac{1}{2}$ per cent. on either side of the theoretical number, and with a tendency to give a result which is a fractional part of a per cent. too high. The majority of the determinations were within half a per cent. of the mean.

Though the results obtained in this manner are accurate, the employment of bromine water as a standard solution was a disadvantage of moment. This led Koppeschaar to try the result obtained by using a solution of a mixture of sodium bromide and bromate, which on the addition of hydrochloric acid yields free bromine according to the reaction—



Direct experiment showed when this mixture was treated with phenol, and excess of hydrochloric acid added, the results were identical with those obtained by the use of bromine water.

In employing a solution of a mixture of sodium bromide and bromate instead of bromine water, the analysis is effected as follows. A solution of five equivalents of sodium bromide and one equivalent of sodium bromate is made of such a strength that 50 c.c. mixed with 10 c.c. of the potassium iodide solution, and, after decomposition, with 5 c.c. of concentrated hydrochloric acid diluted with 100 c.c. of water, requires from 86 to 95 c.c. of the sodium thiosulphate standard solution. Let a = the number of c.c. of the standard solution of sodium thiosulphate required. 25 c.c. of the solution of phenol to be examined (prepared in the same manner as before) is then placed in a quarter-litre flask with a tightly fitting stopper, and 100 c.c. of the standardised solution of the mixed sodium bromide and bromate is added. 5 c.c. of concentrated hydrochloric acid is then quickly run in, the stopper inserted, and the flask well shaken for some time. After standing for a quarter of an hour the flask is opened, and 10 c.c. of the potassium iodide solution is added, the stopper replaced, and the whole agitated, and then left to itself for a short time. The contents and washings of the flask are transferred to a beaker, and the iodine estimated as before with standard sodium thiosulphate. Let b = the number of c.c. of the solution of sodium thiosulphate employed. Then the percentage of phenol in the creasote oil examined is found from the simple expression—

$$\text{Percentage of phenol} = 0.61753 (2a - b).$$

Test experiments are quoted which show the accuracy of the results obtained by this method, four experiments giving 99.2, 99.5, 99.3, 99.5, instead of the theoretical 100. When the sodium salts are replaced by the potassium salts, the different results were found to be slightly more divergent. Of ten experiments, none were more than three-fifths of a per cent. from the mean, or 1 per cent. from the theoretical number. E. N.

Detection of Rosolic Acid in presence of Fuch sine. By P. GUYOT and R. BIDAUX (*Compt. rend.*, lxxxiii, 982—984).—When a solution containing rosolic acid is treated with ammonia, a charac-

teristic rose tint is observed, but if, instead of ammonia, an acid be added, the original claret colour of the rosolic acid disappears, giving place to a yellowish hue.

These reactions being directly contrary to those characteristic of fuchsine, the presence of rosolic acid in wine is likely to cause much embarrassment to the analyst in testing for the former substance.

The fact that ether does not take up rosolic acid from an ammoniacal solution renders it easy to separate the two bodies. The wine to be tested is treated with ammonia and then shaken up with ether, whereby the whole of the fuchsine is removed from the aqueous layer, but none of the rosolic acid. On separating the ether, the presence of fuchsine may be tested by the addition of acetic acid, which produces a rose colour, or by putting into the ether a piece of gun-cotton, which fixes the colouring matter, and with which the tests for fuchsine may be made. The aqueous layer, on the other hand, loses the red colour due to the rosolic acid on the addition of acetic acid.

If the liquid containing the two substances be rendered acid with acetic acid, instead of alkaline with ammonia, the ether takes up both the fuchsine and the rosolic acid, and if to this ether a few drops of ammonia be added, the ether is completely decolorised, while the ammonia separates the rosolic acid, by which it is coloured rose.

F. D. B.

New Tests for Anthracene. By J. BENNETT (*Chem News*, xxxiv, 279).—One gram of anthracene is heated in a flask, to which is fastened an upright condenser, with 45 c.c. of glacial acetic acid; 21 c.c. of an oxidising mixture (100 grams chromic acid dissolved in 50 c.c. glacial acetic acid and 50 c.c. water) is then added, and the whole boiled. The quinone thus separated is washed and dried, and then treated with sulphuric acid (sp. gr. 1.84) until it becomes a crystalline mass. It is then diluted with water, washed on a weighed filter with a 1 per cent. boiling solution of potash, washed again with water, and finally dried and weighed. From the weight of quinone thus obtained the ash after ignition is to be subtracted, and the amount of pure anthracene calculated from the remainder. Another method is to heat the above mixtures together for two hours, leave the whole to itself for twelve hours, then dilute with water, filter, wash the precipitated anthraquinone with potash, and finally with hot water. The anthraquinone is then dried, and dissolved in ten times its weight of concentrated sulphuric acid, and heated until it becomes crystalline. The rest of the process is described above. Anthraquinone is calculated into pure anthracene by multiplying the anthraquinone by 0.856.

E. W. P.

Testing of Quinine Salts for Strychnine and Morphine. By H. HAGER (*Chem. Centr.*, 1876, 90).—The test which the author proposes, as a short and very suitable one for detecting the presence of these poisons in quinine salts, is as follows:—For the valuation of quinines it is generally the custom to dissolve a few decigrams in con-

centrated sulphuric acid, and to confirm the presence or absence of salicin or other bitter principles. In order to apply this solution simultaneously for detecting strychnine and morphine, it is necessary to use about 0.3 gram taken from various parts of the bulk sample, and to dissolve it in about 6 c.c. of pure concentrated sulphuric acid in a test-tube, shaking the latter moderately. A few c.c. of the colourless or slightly yellowish solution are then poured over small crystals of bichromate of potassium. In the case of pure solutions the liquid remains unaltered for a minute, after which the crystals begin to dissolve, whereas when strychnine is present blue streaks immediately spread out from the crystals through the liquid, and afterwards assume a violet, then a red, and finally a green colour. The remainder of the quinine solution is treated with four to five drops of nitrate of silver, and agitated gently. If morphine is present, an immediate reddish-brown coloration sets in, and the solution when warmed assumes a deep reddish-brown colour. It scarcely needs mentioning that substances other than morphine will produce a similar reaction; this reaction, however, is sufficient proof for rejecting the parcel. With the hydrochloride of quinine a separation of white chloride of silver is formed simultaneously, but if morphine is present the reddish-brown coloration is nevertheless visible.

D. B.

Some Reactions of Vegetable Poisons. By O. PAPER (*Arch. Pharm.* [3], viii, 233—234).—The transient colours produced by sulphuric acid and alkaloïds can be rendered more permanent by addition of wheat-starch. Digitalin mixed with ten times its weight of starch and a few drops of sulphuric acid turns blackish-brown; on addition of a few drops of nitric acid and some water, a deep green colour is produced; with cane-sugar it shows the same reaction, but the colouring matter easily dissolves in the water. Both amorphous and crystalline digitalin give substantially the same reaction with starch; with sugar, sulphuric acid turns it yellow, then orange, and finally brown. On addition of water the colour disappears. If hydrochloric acid be substituted for nitric acid, a green colour is also produced. Veratrine with ten times its weight of starch and a few drops of sulphuric acid turns brownish-yellow, and finally brownish-red, and on addition of nitric acid turns yellow. Morphine gives no colour with sulphuric acid alone, but on addition of nitric acid, it gives a fine orange colour. The starch may be advantageously used in testing for codeine, narcotine, narceine, and brucine, but not for strychnine.

W. R.

Detection of Fuchsine and other Colouring Matters. By A. BÉCHAMP (*Compt. rend.*, lxxxiv, 131—133).—The author gives a process for detecting fuchsine and other aniline-colours when fraudulently employed: First, in caramel-colouring: precipitate by addition of lead salt, suspend the precipitate in water, pass sulphuretted hydrogen, and boil the precipitate with alcohol, which will extract all the fuchsine. Secondly, in wine: to 25 c.c. add strong baryta-water to pale green colour; warm gently; filter and wash with weak baryta-water. Acidify a portion of the filtrate with acetic acid, when if

fuchsine be present, the liquid becomes rose-red, and will dye silk. The remainder is to be agitated with twice its volume of ether, and the separated ether, on the addition of a drop of dilute acetic acid will show a vivid coloration if fuchsine be present. R. R.

Detection of Fuchsine in Wines. By G. M. FORDOS (*Compt. rend.*, lxxxiii, 980—981).—Ten c.c. of the wine are shaken with 1 c.c. of pure ammonia, 5 to 10 c.c. of chloroform are then added, the whole well shaken, and the chloroform, after separation by a tap-funnel, heated in a porcelain dish with a piece of white silk immersed in it; when the chloroform is nearly evaporated, a little water is added, and the heating continued. All the fuchsine is thus fixed in the silk which becomes more or less rose-coloured if fuchsine is present.

This method permits of the detection of extremely small quantities of fuchsine, especially if the wine be concentrated, and a very small piece of silk be used. Quantitative results might be obtained by means of a series of pieces of silk coloured more or less deeply, with which the piece coloured by the wine under examination might be compared. F. D. B.

Fuchsine in Wines. By J. FORDOS (*Compt. rend.*, lxxxiii, 1045, 1047).—The modifications which the author here makes of his former process are intended to render it sufficiently easy of execution for industrial purposes. To 10 c.c. of the wine to be tested for fuchsine 1 c.c. of ammonia, and 10 c.c. of chloroform are added. The test-tube is to be several times inverted, but not shaken, and the chloroform drawn off by means of a tap-funnel; a little water is added to it, and then it is saturated with acetic acid. The fuchsine now separates from the chloroform, and its aqueous solution floats on that liquid. Another modification is to use only 5 c.c. of chloroform, and when this has settled to the bottom of the tube, to drop in a crystal of citric acid. The ammonia being saturated, the fuchsine appears on the crystal. R. R.

Dilution of Wines. Influence of Plastering, Fining, Brandy-ing, &c., on the Weight of the Dry Extract. By A. GAUTIER (*Bull. Soc. Chim.* [2], xxvii, 7—17).—When skilfully done, it is generally very difficult to detect the addition of water to wine naturally rich in alcohol, for the purposes of fraudulent adulteration. Generally the expert founds his judgment on the low percentage of dry extract and of glycerin, but grave sources of error may creep in if care be not taken.

In the determination of the extract, it is usual to evaporate the wine at 100°, and then dry the residue on the air-bath; but inaccurate results are obtained in this way, owing to loss of glycerin, &c., and to the alteration of the tannin and nitrogenous matters. These sources of error, however, are entirely avoided by evaporating to dryness and drying in a vacuum for several days at the ordinary temperature; no alteration taking place after 96 hours at 25—32°. As might be expected, the results thus obtained are always higher than those obtained by the ordinary method. The influence of plastering on wine is to raise the amount of extract by about 3.0 to 3.8 grams per litre, the

"Vins du Midi" being raised from 18.2 grams extract per litre to 21.5 to 23.8 grams. The effect of fining on the weight of the dry extract is to diminish it, whether gelatin or white of eggs be employed, since the tannin becomes precipitated; and brandying has the same effect, not only because it increases the volume of the wine without adding any solid material, but also because it precipitates, after a time, certain substances dissolved in the wine, especially the acid potassic tartrate. The stoppage of the fermentation by means of sulphurous acid, alcohol, or salicylic acid retains a portion of the glucose, and so increases the amount of extract. In order to ascertain whether a wine has been diluted, it is necessary to determine the amount of extract, and compare it with wines of the same vintage and same year, having special regard to the amount of tannin and glycerin, and also whether the wine has been plastered, which is easily ascertained by its giving a precipitate with barium chloride, and by the ash being neutral if it has not been mixed with unplastered wines. If the proportion of glycerin is small, whilst the extract is normal, it is probable that the wine has been diluted with washings of the marc from which the wine was made, as this would introduce appreciable quantities of colouring matter, cream of tartar, and tannin.

C. E. G.

Identification of Foreign Colouring Matters in Red Wine. By HILGER (*Chem. Centr.*, 1876, 619).—The colouring matters employed for adulterating red German wines are generally the bilberry, mallow, kermes and fuchsine solution. The reactions obtained according to the following table are sufficient to detect their presence:—

	Hydrogen (Zn + HCl).	Ammonia.	Concentrated potash solution.	Copper sul- phate.	Amyl alcohol.
Mallow ...	Decolorised after short time	Green, gra- dually changing to yellow	Brown	Deep blue	Dissolves on shaking a red colouring mat- ter, which, at the junction of the layers, ap- pears violet.
Kermes (Phyto- lacca)	Decolorised after 12 hours	Changes im- mediately to yellow	Changes im- medi- ately to yellow	Coloured dark brown, changing to green	No colouring matter dis- solved.
Bilberry ..	Slowly de- colorised after 12 hours	Coloured first violet, then gradually changing to red, and finally to brown		Violet	All colouring matter dis- solved.
Fuchsine..	Immediately decolorised	Decolorised	Decolor- ised	—	All colouring matter dis- solved.
Pure red wine	Decolorised gradually	Gradually, changes to brown		At first no action, then gradually changes to brown	Small amount of red colouring matter dis- solved.

E. W. P.

Determination of the Residue of Wine. By L. MAGNIER de la SOURCE (*Bull. Soc. Chim.* [2], xxvi, 488—490).—The residue obtained by evaporating wine at 100° in the ordinary way, does not exhibit a constant weight even after prolonged heating. By effecting the evaporation in a vacuum, the changes induced by the higher temperature are avoided, and the results become comparable, as the differences of the weighings are then much smaller. Several days are, however, required to obtain nearly constant weights. R. R.

Detection of Mineral Acids in Vinegar. By STROHL (*Arch. Pharm.* [5], 4, 342—346).—Calcium oxalate is insoluble in acetic acid, but is dissolved by mineral acids. $\frac{1}{2}$ c.c. ammonium oxalate solution and $\frac{1}{2}$ c.c. calcium chloride solution, each containing $\frac{1}{4}$ equivalent in 1000 c.c. of water, are added to 50 c.c. of the vinegar under examination: if the turbidity which is at first produced does not disappear, the liquid contains less than—

2.85 gram ordinary hydrochloric acid of 1.174 sp. gr. per litre,
 or 4.40 " nitric " 1.33 " "
 or 1.70 " sulphuric " 1.843 " "

M. M. P. M.

Composition of Coffees. By O. LEVESIE (*Arch. Pharm.* [5], 4, 294—298).—The author sought to determine whether the analysis of a sample of coffee would enable one to determine the quality and relative price. So far as his determinations extend, there appears to be no connection between the commercial quality and chemical composition. The following numbers are given:—

	Gummy matter.	Caffein.	Fat.	Tannic and caffeinac acids.	Cellulose.	Ash.	Potash.	Phosphoric acid.
Finest Jamaica plantation.....	25.3	1.43	14.76	22.7	33.8	3.8	1.87	0.31
Finest green Mocha .	22.6	0.64	21.79	23.1	29.9	4.1	2.13	0.42
Ceylon plantation ...	23.8	1.53	14.87	20.9	36.0	4.0	—	0.27
Washed Rio.....	27.4	1.14	15.95	20.9	32.5	4.5	—	0.51
Costa Rica	20.6	1.18	21.12	21.1	33.0	4.9	—	0.46
Malabar	25.8	0.88	18.80	20.7	31.9	4.3	—	0.60
East Indian	24.4	1.01	17.00	19.5	36.4	—	—	—

M. M. P. M.

Testing Roasted Coffee for Chicory. By A. FRANZ (*Arch. Pharm.* [5], 4, 298—302).—An infusion of pure coffee when treated with copper acetate and filtered, yields a greenish-yellow filtrate: an infusion of coffee containing chicory yields, when similarly treated, a dark red-brown filtrate. The liquid should be examined immediately after filtration, as the colour changes on standing. Ten per cent. of chicory may be readily detected. If 0.3 c.c. copper acetate solution

of 2.5—2.6 per cent. be added to 2 c.c. of coffee extract prepared by treating the coffee with 10 parts of water, the results are very satisfactory. M. M. P. M.

Detection of Foreign Mineral Substances in Flour. By H. VOHL (*Deut. Chem. Ges. Ber.*, ix, 1660—1664).—Large quantities of flour are imported from Holland into the Rhine provinces and Westphalia, adulterated with gypsum, heavy spar, China-clay, chalk, and powdered quartz. A simple and expeditious method of detecting these bodies consists in deflagrating a mixture of the flour with pure saltpetre in a platinum or iron crucible. If a quantitative examination is to be made, potassium and sodium carbonates should also be added, and the mixture should be moistened and dried again before ignition. In either case, the mass obtained is free from carbon, and when cool of a more or less faint green colour, owing to the presence of a minute quantity of manganese. In the case of pure flour, this mass is almost entirely soluble in water. Addition of hydrochloric acid liberates carbonic and nitrous acids. If a precipitate is formed on neutralisation which re-dissolves in excess of acid, silica or a silicate is present. If addition of barium chloride to the acid solution produces more than an opalescent turbidity, earthy sulphates have been added. Turbidity produced by addition of ammonia in excess to the acidified solution, points to admixture with aluminium compounds.

If a precipitate is left on solution of the mass in water, and it is dissolved by dilute hydrochloric acid, chloride of ammonium and ammonia will throw down from this solution a brownish precipitate of phosphates, and, after a time, crystals of ammonio-magnesium phosphate will be deposited on the sides of the vessel.

If the hydrochloric acid solution of the precipitate gives a precipitate with calcium sulphate, heavy spar has been added. If, in the filtrate from the phosphates, oxalate of ammonia gives a white precipitate, the specimen is adulterated with gypsum, chalk, &c.

G. T. A.

Some Reactions of Hæmaglobin and its Derivatives. By C. HUNSON (*J. Pharm. Chim.* [4], xxii, 326—329).—By the action of iodine on hæmaglobin, the latter is resolved into hæmatin and globulin. This fact may be proved both by comparing the absorption-spectrum after the addition of the iodine with that of pure hæmatin, and by observing the reaction itself under the microscope. In the latter case, not only is the actual precipitation of the hæmatin visible, but crystals of the iodide may be obtained by gently warming the substance on the microscope slip, with a drop of glacial acetic acid. These crystals belong to the rhombohedral system, and are generally arranged in a star-like manner, often resembling the form of a Maltese cross.

By treating blood with sodium borate and glacial acetic acid, hæmatoidin results. The crystals of this substance, though apparently belonging to the oblique rhombohedral type, assume, in the microscopic field, such varied and multiple forms of arrangement that any description of their appearance would be valueless; it is, how-

ever, noticeable that closely surrounding the crystals, granulations of a peculiar reddish colour always occur, which seem to result from the precipitation of the iron of the hæmatin at the moment of its conversion into hæmatoidin.

With sodium sulphhydrate, colourless or straw-yellow needle-shaped crystals may sometimes be obtained. Ammonium sulphhydrate, however, gives no crystals, but communicates, sometimes, to old blood-stains, the well-known colour produced by a sulphocyanate and a ferric salt. Potassium cyanide or ferrocyanide, and mercury cyanide, also produce crystalline compounds, though the reactions are not effected so easily as those previously mentioned. They succeed best with blood which has been kept for some time, in which, owing to partial putrefaction, the globulin of the hæmaglobin is destroyed. In such case acetic acid alone, without the addition of any other reagent, will give a fine crystallisation of hæmatin acetate; and generally the crystals of the other compounds of this substance are found to be larger in size and more regularly arranged.

Respecting the foregoing communication, M. Hénocque remarks (*ibid.*, 329—331), that the iodine reaction of M. Husson for the detection of blood-stains, is preferable to the method devised by Teichmann, in which crystals were obtained by the action of sodium chloride and acetic acid, since the new process combined much greater precision in working with greater certainty of success. He is of opinion that the microchemical, micrographical, and spectroscopic methods of research should be used simultaneously, for no one process can at present be relied upon as infallible, and in investigations of this nature, it is especially necessary to accumulate proof. He alludes briefly to the recent discussion between Richardson and Woodward, in which it has been distinctly pointed out that the measurement of the red corpuscles does *not* serve to distinguish human blood from the blood of the domestic mammifera, and suggests, therefore, that the action of iodine upon the blood of these animals should be tried, in order to see whether the hæmatin-derivatives so obtained present any characters which may tend to differentiate them from the corresponding compounds obtained from human blood.

J. W.

Testing Aqueous Liquids for Blood. By V. SCHWARTZ (*Arch. Pharm.* [5], 4, 302—323).—The author made use of Teichmann's test, viz., production of hæmin crystals, the spectrum reaction, and the guaiacum test, as carried out by Liman; he also determined the best precipitant for blood dissolved in aqueous liquids. In applying the hæmin test, the author allowed the acetic acid to evaporate spontaneously, he then obtained better results than by heating the slide before placing it under the microscope. The guaiacum test was carried out exactly as described by Hünefeld: the author agrees with Leman in saying that if this test leads to negative results, we may conclude that blood is absent, but that positive results do not certainly indicate the presence of blood. Zinc acetate is generally the best precipitant for blood. One part of blood in 6,000 of water could be precipitated, and the hæmin crystals obtained: 1 in 15,000 could

be detected by the spectroscope after precipitation. In water containing 17 per cent. of common salt, blood could be detected by the hæmin test (after precipitation by means of zinc acetate), only when present in the proportion of 1 to 750. One part of blood was detected in 5,000 parts of soapy water by the spectroscopic and the hæmin tests, after precipitation with tannin solution. With zinc acetate, blood could only be detected when the proportion was 1 to 750 of soapy water. Small quantities of blood could not be satisfactorily detected by these tests when dissolved in urine.

One c.c. of blood was dissolved in 1,500 cb.c. of water (the water used was from a river). The blood could be detected, after precipitation by zinc acetate, by the hæmin or spectroscopic test after 8 days, but by the hæmin test only, after 10 days. The precipitate, with zinc acetate, was carefully washed with distilled water.

Small quantities of blood were detected in linen by treating with potassium iodide solution, precipitating with zinc acetate, and treating the precipitate with salt and acetic acid. This process may be applied to the detection of blood-stains which have been already partially removed by washing and rubbing.

M. M. P. M.

Analysis of Soap. (*Chem. News*, xxxv, 2).—The soap to be analysed should be a slice cut through the bar, at right angles to its length (60—80 grams, dissolved in distilled water, and the volume made up to 1,000 c.c.; of this 50 c.c. are employed for each operation). The total alkali is determined by adding standard acid to 50 c.c. of solution diluted to 200 c.c., and coloured faintly with eosin: the disappearance of colour marks the point of neutrality.

To determine uncombined alkali, 50 c.c. are added to 300 c.c. of saturated sodium chloride solution, and the whole diluted to 400 c.c.: the neutral alkaline salts are precipitated, from which the *combined* and *uncombined* alkali may be calculated. When 50 c.c. of solution of soap are decomposed by acid, and the whole shaken up with carbon disulphide, the disulphide evaporated off, and the residue dried at 100°, the whole quantity of fatty acids is obtained. These, consisting principally of oleic acid, are separated by this process as hydrates, and their weight must be multiplied by 0.97 to obtain the amount of anhydrous acid.

When "olein" soaps of commerce are to be analysed, 50 c.c. of the solution are decomposed in a flask with a long neck, graduated in c.c., so that, on the addition of acid, the whole of the separated acid may rise up into the neck and the volume read off: this volume, multiplied by spec. gr. (0.9) gives its weight.

If the soap be pure, 50 c.c. of solution are evaporated to dryness on the water-bath, and finally dried in a weighed dish; from the weight of anhydrous soap, the quantity of water is calculated. If the soap be cut into thin shavings, and these weighed and dried, the amount of water found falls short of the true amount by 1 or 2 per cent. Should mineral impurities and unsaponified fat be present, they may be detected by dissolving the anhydrous soap in alcohol, and filtering through a hot funnel, the mineral impurities remaining on the filter: the alcoholic filtrate is evaporated with successive additions of

distilled water. The unsaponified fat or resin remains undissolved in the alcohol.

E. W. P.

Technical Chemistry.

Photography. Investigations on Iron-developers. By RORTIER and WALDACK (*Chem. Centr.*, 1876, 90).—These investigations were carried out with the view of ascertaining which are the substances most suitable for the composition of iron-developers, and what are the conditions under which they give the most favourable results. All the experiments were made on the wet collodion process, and in each experiment two negatives were prepared under the same conditions and treated with different developers. In order to obtain two equally latent images, a stereoscopic apparatus with a glass plate of 19 by 11 cm. was employed, the objects taken being the same in each case. After exposure to light in the camera, a strip of glass was placed in the middle of the layer, and first one half of the plate developed, then the other half. In another experiment the glass was scratched along the middle by a diamond, and after preparation and exposure broken in half. The following observations were made:—

1. *Influence of a Concentrated Iron Solution.*—It was found that while a dilute solution developed slowly a thin transparent violet image, concentrated solutions gave at once dark dense pictures. A weak solution penetrates through the layer of the collodion, producing a precipitate of silver throughout the whole of its thickness, while a concentrated solution yields an image only on the surface of the layer. The stronger the solutions the stronger are the negatives. The manner in which the development takes place, apart from the concentration of the solution, influences the consistency of the precipitate to some extent, different results being obtained accordingly as the developer is left at rest on the glass, or moved up and down it.

2. *Influence of Acids.*—In the above-mentioned experiments solutions of ferrous sulphate without addition of acid were used. It is known that the development of images is retarded by acids, different acids showing different results. Organic acids in general produce black precipitates, excepting acetic acid, which gives a very clean negative, and is of great value to the photographer. Glacial acetic acid, commercial acetic acid, and wood-vinegar all give the same results. Sulphurous acid yields a worthless picture, whilst the action of sulphuric acid is as advantageous as that of acetic acid. The greater the quantity of acid used with the developers, the less quickly is the photograph developed, and the weaker is the negative obtained.

3. *Influence of Various Iron Salts.*—With salts other than ferrous sulphate, different results are obtained. With regard to the fineness and strength of the images obtained, the following order is given:—
1. *Ferrous nitrate* develops weak images. 2. *Ferrous sulphate*. No difference is perceived in the results of this preparation, either obtained

from the metal or from its ores by the action of sulphuric acid. 3. *A mixture of equivalents of ferrous sulphate and cupric sulphate* acts in the same manner as ferrous sulphate alone. 4. *Ammonio-ferrous sulphate*. This salt has a more advantageous action than ferrous sulphate, less time being required for exposure. 5. *Ferrous acetate* is to be preferred to the former, as it requires still less time of exposure to the light.

4. *Observations regarding the Use of Ferrous Acetate*.—By adding a small quantity of ferrous acetate to the ordinary iron-developer, its sensitiveness is increased very considerably, intense negatives of harmonious tone being obtained. With too large a quantity of the acetate, however, a confused photograph is obtained. Indeed, the extraordinary sensitiveness of this salt, which enables it to produce negatives of great intensity, renders its action on the other hand too rapid for the development of powerful pictures. D. B.

Preparation of Soluble Glass from Fossil Meal. By F. CAPITAINE (*Dingl. polyt. J.*, cxxii, 363—366).—The use of fossil meal for the preparation of soluble glass was proposed twenty years ago (*Dingl. polyt. J.*, 1857, 143, p. 210 and 237), but has not yet been adopted to any great extent, soluble glass being prepared in England where flint is cheap and abundant, by boiling flint in caustic lyes, and on the Continent by first preparing a glass by fusing sand, soda, sulphate and coal, and then dissolving it in water under pressure.

When flint is boiled with caustic lye of 1.25 to 1.3 sp. gr. for six to eight hours at a pressure of $4\frac{1}{2}$ to 6 atmospheres, it yields a strongly alkaline glass, the proportion of alkali to the silicic acid being about 1 : 2. Fossil meal on the contrary, when boiled for three to four hours with lyes of 1.2 sp. gr. at a pressure of 3 atmospheres, gives a much more neutral product, the quantity of silicic acid in which is three times that of the alkali. It is of course necessary to calcine the meal before treating it with caustic alkali, but as it is necessary to remove all traces of undecomposed organic impurities, the calcination process is rather long and troublesome. As the meal is now, however, brought into commerce in a calcined state and at proportionately lower prices, the author was induced to undertake a series of experiments on a large scale. He used caustic soda solutions of 1.22 to 1.24 sp. gr. An agitator was filled to about 60 per cent. of its volume with this solution, and calcined fossil meal added, using 1 part by weight of sodic hydrate to 2.8 parts by weight of pure fossil meal. The mixture was then agitated for three hours at a pressure of 3 atmospheres, and the operation, i.e., complete solution of silicic acid, finished, when a portion from the agitator settled very quickly.

Too concentrated solutions, of sp. gr. 1.3, for example, gave unsatisfactory results, the clarifying process being retarded while the specific gravity of the product was too high. To obtain potash glass the boiling must be continued for 1—2 hours longer, and 10—15 p.c. more meal used. D. B.

Use of Soluble-glass in the Textile-industry. By H. GROTHE (*Chem. Centr.*, 1876, 92—93).—This paper was worked out by the

author based on van Baerle's accounts regarding the prospects and practical uses which this substance at the present time affords to commerce.

1. *Soluble Glass used in the Textile industry and in the Paper Manufacture.* a. *For domestic washing purposes.*—The action of this composition depends upon its rapid and energetic solution of the sweat and fat through which particles of dirt adhere to materials. It serves therefore not exactly for washing, but for loosening the dirt, by the energetic dissolving action of the soda. A hot solution of the composition also takes up sweat, fat, and tannin from the skin of the hands when the cloths are rubbed in it. Although the material is freed from sweat and fatty ingredients, its fibre and colour is not attacked. This composition is used in the following manner: The articles, without previous soaking, are placed in a lukewarm solution of the composition (a tub holding from 6 to 10 pails requires 1 lb. of composition), covered with a cloth or lid, and kept in this solution over-night. The next morning the whole is stirred up with a stick and the dirty liquor run off. The articles (linen or cotton, either coloured or white) are then treated with a hot solution of 1 to 2 lbs. of composition, stirred up, taken out separately, steeped in a tub of lukewarm water, and if they show signs of dry dirt (fat or sweat no longer present), they are washed or brushed with common fat-soap. Linen or cotton, if free from albuminous substances (blood, pus, nasal mucus), may at once be treated with a very hot solution of composition. Woollen and silk articles may be treated in a similar manner, using a warm solution for the former, and a lukewarm solution for the latter. Woollen articles do not shrink after this treatment. Coloured woollen or silk articles are washed with lukewarm water; white, woollen, or silk materials with cold water, after having been previously pressed. Materials treated with soluble glass are always without smell, much cleaner, and never yellow in colour.

b. *For bleaching.*—The use of soluble glass as a bleacher will become of great importance in the future. The author's experiments made in large bleach-works lead him to the conclusion as destined to supersede soda in bleaching operations. Substances like jute (Calcutta hemp), which hitherto could not be bleached without injuring their fibres, are bleached successfully by the following method: Jute materials are placed in a hot solution of soluble glass at 70°–80° R. for 15 to 20 minutes (using 100 lbs. of water for 6–8 lbs. of soluble glass), and stirred up with a stick; they are then washed in hot water (not boiling), afterwards in cold water, bleached in a weak chlorine-bath, and lastly in an acid bath. Jute thus bleached will doubtless be available not only as a fine white pulp for the paper manufacture, but also for the manufacture of fine white spun-goods. Instead of boiling hemp and cotton-yarns for 6 to 8 hours in a concentrated soda solution, they need merely be moved about in a very hot bath of soluble glass for 10 to 15 minutes; 100 kilos. of linen-yarn require 12–15 kilos. soluble glass, the cost of which is 30 per cent. less than the 10 kilos. of 90° B. calcined soda solution generally used. All the baths may be used for three operations.

c. *For finishing linen or cotton goods in place of China-clay.*—Soluble

glass is preferable for this purpose to China-clay, as it is whiter in colour, and can be formed by chemical reaction in the finest fibres of textures. In order to obtain the precipitate, a piece of linen or cotton is passed through a hot solution of alum and then through a hot solution of soluble glass, to which a small amount of glycerin is added. After this the material is passed through a weak starch-bath, and then through warm cylinders.

d. For impregnating.—Packing cloth, jute-mats, &c., may be rendered fire-proof, and materials used for covering waggons, tents, &c., may be made waterproof, by impregnating them with a solution of soluble glass. D. B.

Extraction of Sulphur. (*Chem. Centr.*, 1876, p. 34).—Native sulphur is usually associated with gypsum. When sulphur and gypsum are heated together to 130°, the gypsum is dehydrated; at 440° or so the anhydrite is reduced to calcium sulphide by the action of the sulphur.



In the ordinary process of sulphur distillation, this reaction doubtless takes place. Chalk exerts a more prejudicial action than gypsum. M. M. P. M.

Extraction of the so-called Soluble Phosphoric Acid from Superphosphates. By H. ERLENMEYER (*Deut. Chem. Ges. Ber.*, ix, 1839—1840).—The author remarks that one part of acid phosphate of calcium is soluble in two parts of water, and that the same salt is decomposed by a small proportion of water into free phosphoric acid and insoluble diphosphate of calcium.

This renders Märker's process (*Zeitschr. f. Anal. Chem.*, 12, s. 275) for the extraction of phosphoric acid applicable with accuracy only to those superphosphates which contain enough free phosphoric acid to prevent the above decomposition. The same applies also to the method of digestion hitherto used for the same bodies. C. L. F.

Dephosphorisation of Iron Ores (Jacobi's Method). By A. GAUTIER (*Chem. Centr.*, 1876, 169).—Jacobi published this method in 1870, and since that time he has used it at the Adalbert foundry at Kladno. Gautier inspected these works and gave the following accounts: The ores which are worked up at Kladno contain, after being roasted, 1½ p.c. of phosphorus. The roasted ore is placed in large tanks, the sides of which consist of wooden boards. They hold 10,000 cwts. Iron pyrites is roasted in furnaces with horizontal bottom, similar to those used in the manufacture of sulphuric acid; the sulphurous acid is condensed with water in separate apparatus, and then passed into the lixiviating vessels. This solution is left in contact with the ore for 24 hours, after which the vessel is emptied and the liquid run through an iron worm, where it is heated to 80 or 90°C. The excess of sulphurous acid escapes, yielding about 80 per cent. of the originally prepared quantity. The liquid is transferred to another vessel, where it deposits impure phosphate of alumina in the form of a white

powder. The average composition of the roasted ore before and after dephosphorising is as follows:—

	Before.	After.
Iron	43 p.c.	46 p.c.
Alumina ..	14—18	6—8
Silicic acid .	14—16	20—22
Phosphorus.	1½	¼

During the working, samples were drawn which gave the following percentages of phosphorus:—

	Ore.	Raw iron.	Puddled iron.
Raw ore	1.1—1.2	1.7—2.1	0.8—0.9
Ore treated with sulphur- ous acid.....	0.2—0.3	0.5—0.6	0.1—0.2
Ore washed with water..	0.5—0.6	1.0—1.1	—

Dephosphorisation takes place to a considerable extent when the ore is lixiviated merely with water. Since the ore is siliceous, sulphuric acid and sulphates are formed, which dissolve the phosphates in presence of water. The object of this very simple lixiviating process is to produce a carboniferous raw iron (foundry-pig); the sulphur facilitates the solution of carbon and renders the formation of a grey pig difficult.

D. B.

Flooring Slabs. (*Chem. Centr.*, 1876, 93).—For several years flooring-slabs have been used in Berlin which, although they do not possess the great hardness of the well known "Mettlach flags," are, nevertheless, very suitable for flooring purposes on account of their durability and their pleasing colours. These slabs are obtained from various establishments on the Rhine and in Lorraine, and if well finished show either a fine straw-yellow, or a deep black colour. Seger thought it advisable to ascertain whether the material had been dyed black by additions of metallic bodies, or whether in its preparation the "steaming" method had been employed. He therefore analysed a yellow and also a black specimen, with the following results:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	C.	Alkalis and loss.
Yellow	51.84	19.71	2.34	—	traces	23.35	0.60	—	2.16 = 100.00 p.c.
Black	52.87	19.75	—	1.97	traces	22.88	0.45	0.36	1.61 = 100.00 „

These numbers show that the black colour is not produced by addition of colouring matters, since in both cases the composition is nearly the same. The black colour, therefore, must have been obtained by steaming, and judging from the small amount of iron, the presence of carbon, and the regularity of the black coloration, it seems highly probable that the blackening was carried out in moulds surrounded by powdered fuel.

D. B.

I. A. R. I. 75.

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